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Report RMD-AOR-ATS-63

(U)

ADVANCED OXIDIZER RESEARCH

COMBINED REPORT

Projects 076, 5007, 5017, 5009 and 5031

February 1964

Research reported in this publication was supported by the Advanced Research Projects Agency.

Thiokol
CHEMICAL CORPORATION
REACTION MOTORS DIVISION
DENVILLE, NEW JERSEY

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ADVANCED OXIDIZER RESEARCH

February 1964

Report RMD AOR-ATS-63

~~Report Period~~ 1 January ~~1963~~ to 31 December 1963

Contract No. NOnr 1878(00), ARPA Order No. 186
Contract No. NOnr 3664(00), ARPA Order No. 23
Contract No. NOnr 3913(00), ARPA Order No. 354
Contract No. NOnr 3824(00), ARPA Order No. 314
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31 December 1963 shall be used for purposes of downgrading and/or declassification of this document.

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GENERAL FOREWORD

This annual technical summary report was prepared by the Thiokol Chemical Corporation, Reaction Motors Division, Denville, New Jersey, and summarizes work in the area of advanced oxidizer chemistry being conducted at this Division under the sponsorship of the Advanced Research Projects Agency. The work was administered by the Department of the Navy, Office of Naval Research, with Mr. R. L. Hanson serving as Scientific Officer, and was conducted under the following contracts:

RMD Project No.	Contract No.	ARPA Order No.	Title
076	NOnr 1878(00)	186	Difluoramine Chemistry
5007	NOnr 3664(00)	23	Structure-Sensitivity Study
5017	NOnr 3913(00)	354	Stabilization of High Energy Solid Oxidizer
5009	NOnr 3824(00)	314	Inorganic Chemistry of the Oxygen Subfluorides
5031	NOnr 4079(00)	417	Investigation of Chemistry of N_2F_2 and NOF

GENERAL INFORMATION

This report describes research conducted at Thiokol Chemical Corporation Reaction Motors Division directed toward the development of advanced solid oxidizers. The five major tasks on which work has been performed are listed below, together with the objective of each task, and are included as five separate sections of this report.

SECTION I. RMD PROJECT 076 - DIFLUORAMINE CHEMISTRY -

Investigation of the chemical reactions of the organic difluoramines.

SECTION II. RMD PROJECT 5007 - STRUCTURE SENSITIVITY STUDY

Preparation of a series of organic difluoramines for evaluation of the relationship between structure and sensitivity.

SECTION III. RMD PROJECT 5017 - STABILIZATION OF HIGH ENERGY SOLID OXIDIZER -

Investigation of the reactions of NO_2ClO_4 with various ligand molecules in an effort to increase the size of the NO_2^+ cation and thereby improve the stability of NO_2ClO_4.

SECTION IV. RMD PROJECT 5009 - INORGANIC CHEMISTRY OF THE OXYGEN SUBFLUORIDES

Investigation of the chemical reactions of O_2F_2 and other oxygen sub fluorides in an effort to discover new reactions leading to solid oxidizers containing oxygen and fluorine.

SECTION V. RMD PROJECT 5031 - INVESTIGATION OF N_2F_2 AND OF NOF

Investigation of the reactions of two unsaturated N-F compounds NOF and N_2F_2 with inorganic reagents.

This report contains two types of data Research results considered to be sufficiently complete to form the basis of a publication in a scientific journal are presented in preprint manuscript form in the first portion of each section covering a given task, while additional data describing incomplete or inconclusive results are summarized in an appendix to each section.

Section I

RMD Project 076

(U)
DIFLUORAMINE CHEMISTRY

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REACTION MOTORS DIVISION

Section I

DIFLUORAMINE CHEMISTRY

Harry F. Smith

and

Joseph A. Castellano

Report RMD-AOR-ATS-63

RMD Project 076
Report Period: 1 January 63 to 31 December 63

Contract No. NOnr 1878(00)
ARPA Order No. 186
Project Code No. 3910

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This report has been distributed in accordance with a combined LPIA-SPIA Distribution List in effect as of the publication data of this report.

FOREWORD

This section of the annual report describes research conducted during the period from 1 January 1963 to 31 December 1963 on the synthesis and chemical reactivity of alkyldifluoramines (RMD Project 076).

The body of this report presents in manuscript form for publication, where security considerations permit, those studies which have been completed. Progress in those research areas in which the work is not in a finished stage is described in an appendix.

Technical personnel contributing to this research effort include: H. F. Smith (Project Scientist) and J. A. Castellano (Synthesis), and R. Storey, D. Yee, J. Creatura, and A. Fremmer (Instrumental and Wet Chemical Analysis).

ABSTRACT

Tertiary alkyldifluoramines react rapidly with organometallic reagents via a succession of one-electron reduction steps. Products arising from the intermediary ~~nitrogen~~ radical and nitrene ~~have been~~ isolated and identified. Triphenylmethyldifluoramine reacted with n-butyllithium to yield benzophenone anil, apparently by a rearrangement of the nitrene intermediate.

~~The~~ survey of the reactions of alkyl and olefinic difluoramines with oxidizing agents ~~has been~~ extended and results obtained with ~~potassium permanganate~~ $KMnO_4$ solutions are reported. The attack of concentrated ~~nitric acid~~ HNO_3 on tertiary alkyldifluoramines is ~~shown to be~~ electrophilic, rather than oxidative, in nature.

The synthesis of new isomeric organic difluoramines, by the addition of ~~tetrafluorohydrazine~~ to 1,3-cyclohexadiene, is described. A new technique for controlled dehydrofluorination utilizing a basic ion-exchange resin ~~has been~~ developed and applied to these bis(difluoramines).

A convenient new synthesis of t-butyldifluoramine from t-butyl iodide and ~~tetrafluorohydrazine~~ is described.

CONTENTS

I. INTRODUCTION

The objective of this research program is to investigate the chemical properties of alkyldifluoramines and to elucidate the mechanisms of those reactions which are found to occur. Such information can be applied in the development of useful new synthetic reactions in difluoramine chemistry, as well as in the effective utilization of nitrogen-fluorine compounds in high energy propellant technology.

The scope of the program embraces the reactions of alkyldifluoramines with electrophilic and nucleophilic reagents, with oxidizing and reducing agents, and with atoms and free radicals. The difluoramino compounds examined have been selected from among the extensive assortment of vicinal bis(difluoramines), 1,4-bis(difluoramines) and geminal bis(difluoramines) which have been synthesized as candidate components of high energy rocket propellants (Ref 1). The tris(difluoramines) now becoming available through the use of perfluoroguanidine also fall within the scope of this program and will be considered for future study. In addition, it has in some instances been advantageous to study the reactions of simpler difluoramines in order to avoid a complexity of reaction products which would interfere with the precise delineation of a reaction mechanism (Ref 2).

This report presents the results of completed studies on the reactions of alkyldifluoramines with organometallic reagents and with concentrated nitric acid and a convenient new synthesis of t-butyldifluoramine, which has served as a model compound for much of this research. These are presented in the form of manuscripts of papers for publication in a chemical journal.

The present status of our investigations in two other areas of difluoramine chemistry is outlined in the appendix. This work, directed toward the synthesis of a new bis(difluoramine) and its reactions with nucleophiles and an investigation of the possibility of producing useful new propellant ingredients by the permanganate oxidation of olefinic difluoramines, is not yet complete.

II. MANUSCRIPTS OF PAPERS FOR PUBLICATION

The Chemistry of Alkyldifluoramines. I.
Reaction with Organometallic Compounds

The Chemistry of Alkyldifluoramines. II.
Reaction with Nitric Acid

Technical Note

A Convenient Synthesis of t-Butyldifluoramine

Prepared for Submission to
Journal of Organic Chemistry

Thiokol
REACTION MOTORS DIVISION

Contribution from the Chemistry Department, Reaction Motors Division
Thiokol Chemical Corporation, Denville, N.J.

The Chemistry of Alkyldifluoramines. I. Reaction with Organometallic Compounds[1]

Harry F. Smith, Joseph A. Costellano and Donald D. Perry

(1) This work was supported by the Advanced Research Projects Agency and and administered by the Department of the Navy, Office of Naval Research, under Contract NOnr 1878(00).

Tertiary alkyldifluoramines reacted rapidly with organolithium reagents. The products obtained include azo compounds, symmetrical fluorine-substituted hydrazines, mixed tertiary amines, and the hydrocarbons resulting from the coupling of two radicals derived from the organometallic reagent. Triphenylmethyldifluoramine yielded principally benzophenone anil. A mechanism involving two successive one-electron reduction steps, to give nitrogen radicals and nitrenes as intermediates, is compatible with all the products observed.

The first synthesis of an N,N-difluoroalkylamine (alkyldifluoramine) in 1936[2] introduced a new family of organic compounds. The perfluoroalkyldifluor-

(2) O. Ruff and M. Giese, Ber., 69B, 598 (1936).

amines obtained by fluorination of various carbon-nitrogen compounds[3] have

(3) (a) G. E. Coates, J. Harris, and T. Sutcliffe, J. Chem. Soc., 1951, 2762.

(b) R. N. Haszeldine, Research, 4, 338 (1951).

(c) J. A. Attaway, R. H. Groth, and L. A. Bigelow, J. Am. Chem. Soc., 81, 3599 (1959).

(d) L. A. Bigelow, "Fundamental Research in Organic Fluroine Chemistry," Terminal Report, Office of Naval Research, AD No. 207549, 31 August 1958.

(e) R. K. Pearson and R. D. Dresdner, J. Am. Chem. Soc., 84, 4743 (1962).

more recently been supplemented by a limited number of analogous compounds containing nonfluorinated alkyl groups.[4] This paper constitutes the first in a

(4) (a) J. W. Frazer, J. Inorg. Nucl. Chem., 16, 23 (1960).

(b) R. C. Petry and J. P. Freeman, J. Am. Chem. Soc., 83, 3912 (1961).

(c) W. H. Graham and C. O. Parker, J. Org. Chem., 28, 850 (1963).

(d) H. F. Smith and J. A. Castellano, "A Convenient Synthesis of t-Butyldifluoramine," in press.

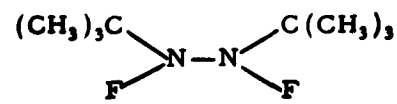
series devoted to the study of the chemical properties of these interesting compounds.

Results

The slow addition of phenyllithium to an equimolar quantity of t-butyldifluoramine (I) in ethereal solution at 0-5° resulted in immediate reaction. The organic phase, after being washed with water, was found to contain biphenyl (50% of theory) and small amounts of azoisobutane (II) and 1,2-difluoro-1,2,-di-t-butylhydrazine (III) identified by infrared and mass spectral analysis. The aqueous washings contained 20% of the total fluorine originally present in I as fluoride ion.

$(CH_3)_3CN{=}NC(CH_3)_3$

II



III

When n-butyllithium in hexane solution was substituted for the phenyllithium, the principal organic product was n-octane. Fluoride ion recovery was 26% in this instance. An increase in the amount of n-butyllithium added, to two moles per mole of difluoramine, resulted in the formation of 49% of the theoretical amount of fluoride. In addition to n-octane, a new organic product, N,N-di-n-butyl-t-butylamine (IV), was obtained. This previously unknown tertiary amine, b.p. 80-82°/0.3 mm. was identified by infrared and mass spectral analysis. A comparison of the mass spectrum of IV with that of tri-n-butylamine (Table I) showed that the major peaks were similar but their relative intensities were quite different. The mass peaks due to rearrangements were generally more intense and two such peaks (m/e = 86, 114), which do not occur in tri-n-butylamine, were observed.

A similar reaction of I with four molar equivalents of n-butyllithium gave IV in 16% yield. The observed increase in fluoride recovery, from 49% to 52%, was probably not significant.

The reaction of triphenylmethyldifluoramine ("trityldifluoramine," V) with one or two equivalents of n-butyllithium yielded only two isolable organic products, n-octane and benzophenone anil (VI). With one mole of n-butyllithium

$$\phi_2C{=}N\phi$$

VI

Table I

Principal Mass Peaks of N,N-n-Butyl-t-Butylamine and Tri-n-Butylamine

m/e	Ionic Species		Relative Intensity (n-Bu)$_2$N-t-Bu	(n-Bu)$_3$N [a]
41	C_3H_5+		90	21.4
42	C_3H_6+		34	16.0
43	C_3H_7+		85	7.8
57	C_4H_9+		100	13.4
58	C_4H_{10} or $C_3H_3NH_2$+	(Rearrangement)	75	5.0
72	C_4H_9NH+	(Rearrangement)	91	1.16
86	$C_4H_9NHCH_2$+	(Rearrangement)	92	4.26
99	$C_4H_9N(CH_2)_2$+	(Rearrangement)	12	---
100	$C_4H_9NH(CH_2)_2$+	(Rearrangement)	8	26.3
113	C_4H_9-N-$(CH_2)_3$+		8	---
114	C_9H_9-NH$(CH_2)_3$+	(Rearrangement)	4	0.25
128	$(C_4H_9)_2N$+		68	1.03
142	$(C_4H_9)_2NCH_2^+$		63	100.0
170	$(C_4H_9)_2NC_3H_6$+		26	0.14
185	$(C_4H_9)_3N$+		8	5.22

a. Mass Spectral Data, A.P.I., Serial No. 1132

reaction was not complete and some V was recovered. The use of two moles of the organometallic reagent caused the complete disappearance of the difluoramine and resulted in yields of the anil up to 70%. Fluoride recovery was 40% and 77% with one and two molar equivalents, respectively. A summary of these data is contained in Table II.

Table II

Reactions of t-Alkyldifluoramines With Organolithium Reagents

RNF_2	R'M	Mole Ratio RNF_2:R'M	R'-R', MMoles	Meq. F^- (% yield)	Organic Products
I	PhLi	1:1	Ph-Ph, N.D.[a]	2.11(21.1)	II, III
I	PhLi	1:1	Ph-Ph, 5.85	7.80(19.5)	Unknown liq. bp 95-110°
I	n-BuLi	1:1	n-C_8H_{18}, N.D.[a]	10.25(25.6)	None identified
I	n-BuLi	1:1	n-C_8H_{18}, N.D.[a]	5.12(26.6)	Unknown liq. bp 150°/0.3 mm, see text
I	n-BuLi	1:2	n-C_8H_{18}, N.D.[a]	9.75(48.8)	Aliphatics, R-COOH
I	n-BuLi	1:4	N.D.[a]	10.40(52.0)	16% IV
V	n-BuLi	1:1	N.D.[a]	16.05(40.1)	V, VI
V	n-BuLi	1:2	n-C_8H_{18}, N.D.[a]	N.D.[a]	42% VI
V	n-BuLi	1:2	N.D.[a]	7.70(77.0)	70% VI

a. N.D. = Not determined

Proposed Mechanism

The various products obtained in the experiments described above can be explained on the assumption that the organometallic reagents reduced the tertiary alkyldifluoramines via a succession of one-electron transfer steps.

$$R_3CNF_2 + R'Li \longrightarrow R_3C\dot{N}F + R'\cdot + LiF \qquad (1)$$

I VII a, $R = CH_3$; b, $R = \phi$

$$R_3C\dot{N}F + R'Li \longrightarrow R_3C\dot{N}\cdot + R'\cdot + LiF \qquad (2)$$

VII VIII a, $R = CH_3$; b, $R = \phi$

A possible alternative for the step shown in equation 2 would be interaction of the R' radical derived from the organometallic reagent with the amino radical (VII). Such a process would also produce the nitrene (VIII), but would require different stoichiometry.

$$R_3C\dot{N}F + R'\cdot \longrightarrow R_3C\dot{N}\cdot + R'F \qquad (3)$$

VII VIII

No trace of the fluorocarbon by-products which would be formed in this process has been detected.

The array of final products obtained in any one experiment was observed, as expected, to depend upon the reactant ratio and the order and rate of addition. The reactive intermediate species are capable of interacting in various combinations and products arising from several of these possibilities have been detected.

In each case the hydrocarbon produced by the coupling of two similar radicals derived from the organometallic reagent was a prominent product. Diphenyl and n-octane were obtained from phenyllithium and n-butyllithium,

respectively. When an equimolar quantity of phenyllithium was added slowly to t-butyldifluoramine (I), the homogeneous coupling product (III) of the amino radical (VIIa) was detected among the products, along with the coupling product (II) of the nitrene (VIIIa). The diradical nature of nitrenes, which leads to

$$2(CH_3)_3C\dot{N}F \longrightarrow (CH_3)_3C\dot{N}\text{-}\dot{N}C(CH_3)_3 \qquad (4)$$

VIIa (F F) III

$$2(CH_3)_3C\dot{N}\cdot \longrightarrow (CH_3)_3N{=}N(CH_3)_3 \qquad (5)$$

VIIIa II

dimerization and the production of azo compounds, is well known.[5] The cross-

5. L. Horner and A. Christmann, Angew. Chem. (Intl. Ed.), 2, 599 (1963).

coupling of VIIIa with the n-butyl radical has been observed when an excess of n-butyllithium was used.

$$(CH_3)_3CN\cdot + 2\ CH_3(CH_2)_3\cdot \longrightarrow (CH_3)_3CN(CH_2CH_2CH_2CH_2)_2 \qquad (6)$$

VIIIa IV

In reactions involving trityldifluoramine (V) rearrangement of the nitrene (VIIIb) appears to be favored energetically, since benzophenone anil (VI) was the only product found. VI has been reported as the principal product of thermal

$$\phi_3CN\cdot \longrightarrow \phi_2C{=}NO \qquad (7)$$

VIIIb VI

decomposition of tritylazide, N-tritylhydroxylamine, and a number of related compounds[6,7,8], presumably also via the nitrene intermediate.

6. Steiglitz, et al., J. Am. Chem. Soc., 36, 272 (1914); ibid., 38, 2081, 2718, 2717 (1916); ibid., 44, 1270, 1293 (1922).
7. L. W. Jones and E. E. Fleck, ibid., 50, 2022 (1928).
8. W. H. Saunders and J. C. Ware, ibid., 80, 3328 (1958).

Experimental

Materials - The phenyllithium and n-butyllithium used in this work were commercial products supplied by Foote Mineral Company in ether-benzene and hexane solutions, respectively. Trityldifluoramine was obtained from Pennisular Chem Research and purified by recrystallization from methanol, m.p. 80-81.5° (uncorr.). t-Butyldifluoramine was prepared by the method of Smith and Castellano[4d] and stored under prepurified nitrogen. The quantity desired for each experiment was distilled from the storage bulb under vacuum and was measured by volume as a gas, assuming ideality. It was condensed directly into the reaction flask from the vacuum line.

Reaction of t-Butyldifluoramine with Phenyllithium

t-Butyldifluoramine (0 55 g., 0 005 mole) was dissolved in 10 ml. of sodium-dried ether and the solution was cooled to 0-5°. In a dropping funnel under nitrogen, 2.5 ml.(0.005 mole) of phenyllithium solution in benzene-ether

(Lithium Corporation of America) was diluted with dry ether to 10 ml. This solution was added to the stirred difluoramine solution during one hour. A red-brown color appeared and deepened gradually during the addition. A gentle stream of nitrogen was passed through the reaction flask and then bubbled into a standardized solution containing 5.27 meq.of acid, while 20 ml.of distilled water was added dropwise to the reaction mixture (20 min.). Stirring was continued for one hour. The acid solution was titrated with base and 5.19 meq. was found. The decrease (1.5%) was not considered to be significant. The aqueous and organic phases of the reaction mixture were separated. The water layer was washed with 15 ml.of ether. The wash and the organic layer were combined and washed with three 10ml. portions of distilled water. These washes were combined with the aqueous solution, which was subjected to analyses as discussed above.

The ether-ben. ne solution was dried first over Drierite and then over anhydrous sodium sulfate and distilled at atmospheric pressure. The flask was heated in a bath at 55-60° throughout distillation of the bulk of the solvents and raised to 95-100° for 20 min. at the end. A brown tarry residue weighing 1.10 g. remained. The distillate was collected at Dry Ice temperature to avoid the loss of unreacted t-butyldifluoramine or low-boiling products. Both fractions were analyzed by infrared and mass spectrometric methods.

The several components of the less volatile fraction were separated by vapor phase chromatography, using a Perkin-Elmer Model 154C instrument. The six-foot column was packed with di-n-decyl phthalate on firebrick and was maintained at 90° with a helium flowrate of 53 ml/min. The effluent stream was fed directly into the inlet of a Bendix time-of-flight mass spectrometer. Mass peaks characteristic of azoisobutane and attributable to 1,2-difluoro-1,2 di-t-butylhydrazine were detected in two different fractions.

Reaction of t-Butyldifluoramine with n-Butyllithium

A solution of 1.1 g. (0.01 mole) t-butyldifluoramine in 10 ml. hexane was treated with 26.0 ml. (0.04 mole) of n-butyllithium solution, by adding the organometallic reagent dropwise over a one hour period at 5-10°. The dark brown mixture was stirred for 2.5 hr. at 10-25° and then treated with water. The organic solution was separated and dried over anhydrous Na_2SO_4 while the aqueous solution was analyzed and found to contain 0.197 g. (0.0104 mole, 52.0%) of fluoride ion. The solvent was evaporated from the organic solution and the residual brown oil was distilled to yield 0.32 g. of a liquid, b.p. 79-82°/0.3 mm. On the basis of infrared and spectral data, the liquid product was identified as N,N,di-n-butyl-t-butylamine.

Reaction of Trityldifluoramine with n-Butyllithium

A solution of 5.9 g. (0.02 mole) of trityldifluoramine, m.p. 80-81.5°C, in 40 ml. of hexane was cooled to 0° in a 200 ml. three-neck flask while 25.8 ml.

(0.04 mole) of n-butyllithium solution was added dropwise with stirring over a 1.5 hr. period. A deep red color developed as the butyllithium came into contact with the hexane solution, but the color changed to a bright yellow on continued stirring at 5-10°. At the completion of the addition, the solution was allowed to come to room temperature and it was stirred at 25° for 2 hr. Water was then added to the mixture, the organic phase was separated, washed with water and dried over anhydrous Na_2SO_4. The solvent was evaporated, leaving 5.72 g. of brown semi-solid. The material was kept under 0.5 mm pressure for 1 hr., a liquid nitrogen trap being employed to collect any liquid distillate. A liquid (0.3 g.) was obtained and submitted for infrared analysis. It showed very strong absorptions indicative of O-H, aliphatic C-H, C-CH_3, C-OH and -$(CH_2)n>4$. In addition, a medium strength band at 1710 $cm.^{-1}$ (C=O) was also present.

The residue was recrystallized from MeOH to yield 2.15 g. (42%) of yellow crystals, m.p. 112-113°, which were identified by infrared and elemental analysis as N-phenylimidobenzophenone (benzophenone anil).

Anal. Calcd. for $C_{19}H_{15}N$: C, 88.68, H, 5.88; N, 5.44.

Found C, 88.85, H, 5.86, N, 5.61.

The physical constants are in excellent agreement with the literature (m.p. 113-114°[9]).

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9. Weston and Michaels, J. Am. Chem. Soc., 73, 1381 (1951).

The methanol solution from the recrystallization was evaporated to dryness to yield 3.3 g. of a mixture of trityldifluoramine and N-phenylimidobenzophenone. In addition, the infrared spectrum of this material showed weak absorptions due to aliphatic C-H, C=O and C=N or C=C.

A solution of 1.48 g.(0.005 mole) of trityldifluoramine in 30 ml. hexane was treated with 6.5 ml. (0.01 mole) of n-butyllithium solution as in Section 1. Water was added to the reaction mixture and the organic phase was separated and washed with four 100-ml portions of distilled water. The combined aqueous washings were transferred to a 500 ml.volumetric flask and adjusted to volume with distilled water. This solution was found to contain 146 mg. F^- (0.0077 mole, 77%) and 0.0028 mole OH^-.

The hexane solution was dried over Na_2SO_4 and the solvent evaporated. The residue was taken up in CH_2Cl_2 and chromatographed on alumina. The chromatogram was followed by the yellow band which moved down the column. This yellow CH_2Cl_2 eluate was evaporated to dryness and the residue was recrystallized from ether to yield 0.92 g.(0.0036 mole, 72%) benzophenone anil, m.p. 112-113°. The column was eluted with MeOH and the solvent was evaporated to give 0.13 g. of brown solid. The infrared spectrum of this material showed strong absorptions indicative of aliphatic C-H, aromatic C-H, C=N or C=O (1660 cm^{-1}), a trace of N-F, and substituted aromatic.

Acknowlegement - The authors wish to thank Mr. Richard L. Hanson of the Office of Naval Research and Dr. Murray S. Cohen of these laboratories for their interest and encouragement during the course of this work. Analytical assistance by Messrs. Alan Fremmer, John Creatura, Raymond Storey and Donald Y. Yee is gratefully acknowledged.

Contribution from the Chemistry Department, Reaction Motors Division, Thiokol Chemical Corporation, Denville, N.J.

The Chemistry of Alkyldifluoramines. II. Reaction with Nitric Acid[1]

Harry F. Smith and Donald D. Perry

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(1) This work was supported by the Advanced Research Projects Agency and administered by the Department of the Navy, Office of Naval Research, under Contract No. NOnr 1878(00).

(2) Previous paper in this series, H. F. Smith, J. A. Castellano, and D. D. Perry, This Journal, ...

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t-Butyldifluoramine was attacked by concentrated nitric acid at room temperature to give a complex array of products including alkyl nitrates and nitrites. With a large excess of acid, oxidation of the organic compound to carbon dioxide occurred. Trityldifluoramine in the presence of excess nitric acid gave triphenylcarbinol as the major product, along with a nitroalkane.

As part of a continuing program of research on the chemical reactivity of organic N-F compounds, we have studied the reactions of two representative

tertiary alkyldifluoramines with concentrated nitric acid. Since this reagent exhibits both oxidative and electrophilic properties, one can anticipate several possible modes of attack. The difluoramine might be protonated and subsequently hydrolyzed, oxidation might produce an amine oxide analog, oxidative cleavage might occur at N-F, C-N, or C-C bonds, or a nitroalkane might be produced. It has been reported, for example, that trityldifluoramine is protonated in concentrated sulfuric acid and decomposes with the liberation of difluoramine[3]. We

(3) W. H. Graham and C. O. Parker, J. Org. Chem., 28, 850 (1963).

have confirmed this observation and found, furthermore, that a secondary alkyldifluoramine is similarly protonated but decomposes with the evolution of hydrogen fluoride[4]. Trityldifluoramine has been found to dissolve in glacial

(4) Unpulished experiments, this laboratory.

acetic acid and to be recovered unchanged upon dilution with water. It was not affected by contact with concentrated hydrochloric acid at room temperature.

The room temperature reactions of t-butyldifluoramine and trityldifluoramine with concentrated nitric acid, both equimolar quantities and large excesses, have been studied. Table I presents a summary of the products obtained in each case, as determined chiefly by infrared spectral evidence.

Table I

Reactions of Alkyldifluoramines with 70% Nitric Acid

	t-Butyldifluoramine		Trityldifluoramine	
Product	Equimolar acid	Excess acid	Equimolar acid	Excess acid
NO_2	---	Large	Present	Large
N_2O	Present	Present	---	Present
CO_2	---	Large	---	Present
NO_3F	Trace	Trace	---	Trace
NOCl or NO_2F	---	---	---	Trace
SiF_4	Present	Present	---	Present
Alkyl nitrate	Present	Present	---	Present
Alkyl nitrite	---	Present	---	Present
Nitroalkane	---	---	---	Present
Carbinol	---	---	---	Major
Alkyl-difluoramine	Present	---	Major	---

Several points are worth considering in some detail. The large amounts of nitrogen dioxide obtained when excess acid was used is apparently the result of catalyzed decomposition of nitric acid. This interpretation is supported by the fact that the quantities of gas obtained were greatly in excess of a stoichiometric

relation with the difluoramine and by the observed exponential pressure rise following a protracted induction period.

The presence of carbon dioxide among the products of the reaction of t-butyldifluoramine with excess nitric acid is a clear indication that C-C bond cleavage occurred. The nitrate and nitrite esters produced in this experiment were mixtures of various alkyl derivatives, and not solely t-butyl derivatives as in the other cases where nitrate esters were detected. The relative stability of trityldifluoramine toward oxidative cleavage is fully in accord with accepted principles.

The appearance of silicon tetrafluoride during an investigation of organic fluorine compounds in glass equipment is generally understood to imply the transient formation of hydrogen fluoride; this interpretation should be applied here. An interesting point, not yet fully understood, is the appearance of nitroalkane and carbinol only in the reaction of trityldifluoramine with excess acid.

In general, the results observed are best understood as the consequences of electrophilic attack on the alkyldifluoramines. The fact that such attack did not occur when trityldifluoramine was treated with hydrochloric acid, an even stronger electrophile, tends to cloud this simple picture. It becomes necessary to invoke the simultaneous participation of an oxidative process in some way which is not yet clear.

Assuming that protonation of the alkyldifluoramine does occur, elimination of difluoramine and formation of a tertiary carbonium ion would logically follow.

$$R_3CNF_2 + H^+ \longrightarrow R_3\overset{+}{C}NF_2H \quad (1)$$

$$R_3\overset{+}{C}NF_2H \longrightarrow R_3C^+ + HNF_2 \quad (2)$$

The failure of difluoramine to appear among the final products is not particularly alarming. In the presence of nitric acid and/or nitrogen oxides, it might easily be decomposed and may well constitute the source of the silicon tetrafluoride.

Reaction of the carbonium ion with water or with nitrate ion would produce the carbinol and the ester, respectively. Alternatively, the carbinol might

$$R_3C^+ + H_2O \longrightarrow R_3COH + H^+ \quad (3)$$

$$R_3C^+ + NO_3^- \longrightarrow R_3CONO_2 \quad (4)$$

be esterified by nitric acid.

$$R_3COH + HNO_3 \longrightarrow R_3CONO_2 + H_2O \quad (5)$$

Experimental

Materials - The t-butyldifluoramine used in this work was prepared by the method of Smith and Castellano[5]. Trityldifluoramine was purchased from

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(5) H. F. Smith and J. A. Castellano, "A Convenient Synthesis of t-Butyldifluoramine," in press.

Peninsular Chem Research and purified by recrystallization from methanol, m.p. 8-81.5° (uncorr.). Nitric acid was Mallinckrodt "Analyzed Reagent."

t-Butyldifluoramine and Nitric Acid

1. t-Butyldifluoramine (1.02 g., 9.3 mmoles) was condensed under vacuum into a flask containing 10 ml. (0.15 mole) of concentrated HNO_3. The mixture was warmed to room temperature and stirred. The pressure rose to 210-220 mm. and remained constant for 16 hr. After this period, the pressure rose within 1-1/2 hr. to 730 mm., with the evolution of brown gas. On cooling the reaction flask to -70°, the pressure dropped to 340 mm. A sample of this gas was subjected to infrared analysis and found to contain C-H (3.33/6.75μ), $C-CH_3$ (7.27μ), N_2O (4.5μ), N_2O_4 (5.72/6.15μ), N-F (attributed to starting material, 10.30/11.35μ), NO_3F (10.85/12.65/13.90μ), CO_2 (4.35/15.96μ), SiF_4 (9.75μ), and NOCl (presumarly from attack on NaCl window, 5.53/5.58μ). Mass spectrometric analysis confirmed the presence of starting difluoramine, CO_2 and/or N_2O, SiF_4, and NO_3F, and established the absence of H_2 and O_2. A second gas sample taken at 0° was found to contain some of these components, but no additional products. The acid solution was extracted with pentane to remove organic products. Infrared analysis of this extract revealed the presence of alkyl nitrite and nitrate (C-H at 3.51/6.90μ, possible $C-CH_3$ at 7.28μ, C-ONO at 6.41μ, and $C-ONO_2$ at 6.10μ).

2. Concentrated nitric acid (0.67 ml., 10.0 mmoles) was delivered by pipet into a 50 ml. round-bottomed flask, which was fitted with a magnetic stirring bar and a suitable adapter, and attached to a vacuum line. The acid was frozen in a liquid N_2 bath and the flask was evacuated. The acid was melted and refrozen twice, with evacuation to effect degassification. t-Butyldifluoramine (1.09 g., 10.0 mmoles) was evaporated into an evacuated calibrated storage bulb to the calculated pressure and then condensed into the flask with liquid N_2. The reactor portion of the line (with manometer) was closed off, and the flask was allowed to warm to room temperature. The mixture was stirred at 26-29° for 24 hr., during which the pressure remained essentially constant (186-198 mm. Hg). The liquid mixture became yellow, but no brown fumes appeared in the vapor space.

Gas samples for infrared and mass spectral analyses were taken, with the reaction flask at 25° and -78°. Both samples contained an alkyl nitrat N_2O, t-butyldifluoramine and some additional N-F material, and a trace of NO_3F.

The liquid reaction mixture was extracted with CCl_4. Infrared analysis of the extract did not indicate any additional products. The aqueous residue was evaporated to dryness at room temperature and a few needle crystals were recovered. The infrared spectrum of this solid showed only absorptions due to water. Attempts to dehydrate the small amount of product which remained were unsuccessful.

Trityldifluoramine and Nitric Acid

1. Recrystallized trityldifluoramine (1.0 g., 3.4 mmoles, m.p. 80-81.5°) and a small magnetic stirring bar were placed in the bottom of a reaction tube having a small side chamber. Concentrated (70%) nitric acid (2.5 ml., 38 mmoles) was placed in the side chamber and the tube was connected to a vacuum line by means of standard taper joints. The nitric acid was frozen by immersion in a liquid nitrogen bath and the system was evacuated. The cold bath was removed. Then the tube was rotated so that the nitric acid, as it melted, flowed onto the trityldifluoramine.

The resulting slurry was stirred at 22-25° for 24 hr. The reaction mixture bubbled and became progressively darker and brown fumes were observed in the vapor space. The pressure rose exponentially to reach a maximum of approximately 400 mm. in 2.5 hr. (system volume - 180 ml.) and then remained constant.

After 24 hr., the reaction mixture was cooled to -78°, and a gas sample was taken for analysis. Infrared and mass spectrometric examination revealed the presence of NO_2, N_2O, SiF_4, and either NOCl or NO_2F.

The reaction tube was then warmed to room temperature, flushed with nitrogen, and opened. The reaction mixture was diluted with distilled water (color changed from dark brown to bright orange) and the solid product was removed by filtration. The filtrate was neutralized with Na_2CO_3 (color

changed from pale amber to brown) and extracted with benzene. No residue was obtained upon evaporation of an aliquot of the benzene extract. Reacidification of the aqueous layer lightened the color, but not to the original shade. The remaining color was too intense to permit the determination of fluoride ion.

The orange solid product was washed with water, dried in vacuum over P_2O_5, and chromatographed on an alkaline alumina column. The first fraction, 420 mg., yellow to pale orange crystals eluted with pentane-benzene, proved to be the principal constituent of the mixture. It was recrystallized from pentane-benzene to give a nearly colorless compound. m.p. 162.5-163°. Its infrared spectrum was identical with that of triphenylcarbinol (lit.[6] m.p. 162.5°).

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(6) N. A. Lange, Handbook of Chemistry

Anal. Calcd for $C_{19}H_{16}O$: C, 87.66, H, 6.20

Found : C, 87.06/87.21; H, 6.29/6.41

2. Trityldifluoramine (2.95 g., 10 mmoles) was placed, along with a small magnetic stirring bar, in a test tube having a standard taper glass joint. The tube was flushed with dry nitrogen and placed in a liquid nitrogen bath. Concentrated HNO_3 (0.67 ml., 10 mmoles) was introduced slowly and allowed to freeze on the side of the tube without contacting the trityldifluoramine. The reaction tube was then connected via a suitable adapter to a vacuum system, evacuated, and allowed to warm to room temperature. After the mixture was

stirred for 18 hr. at 25-28°, a sample of the gaseous products (p =55 mm. in 180 ml.) was taken in an evacuated cell. The system was then filled with nitrogen to atmospheric pressure. The reaction mixture was diluted with distilled water and the yellow insoluble product was removed by filtration. The yellow aqueous filtrate was extracted three times with methylene chloride, the third extract contained very little color, although the aqueous solution remained a strong yellow. On standing, the combined extracts became orange in color, as did the solid product on the filter.

Infrared analyses of the gas sample and the methylene chloride extract (differential vs. solvent) showed no significant absorptions. The aqueous solution was found to contain 7.41 meq. of free acid and 25 mg. (1.3 meq.) of fluoride ion. The infrared absorption spectrum of the bright yellow-orange solid (m.p. 79-81°) was superimposible upon that of trityldifluoramine.

Acknowledgement. The authors wish to thank Mr. Richard L. Hanson of the Office of Naval Research and Dr. Murray S Cohen of these laboratories for their interest and encouragement during the course of this work. Analytical assistance by Alan Fremmer, John Creatura, Raymond Storey and Donald Y. Yee is gratefully acknowledged.

Contribution from the Chemistry Department, Reaction Motors Division, Thiokol Chemical Corporation, Denville, N. J.

A Convenient Synthesis of t-Butyldifluoramine [1]

Harry F. Smith and Joseph A. Costellano

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(1) This work was supported by the Advanced Research Projects Agency and administered by the Department of the Navy, Office of Naval Research under Contract NOnr 1878(00).

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t-Butyldifluoramine (N,N-difluoro-t-butylamine) was required in sizeable quantities for use in an investigation of the chemical properties of alkyldifluoramines. A reported synthesis[2] of this compound capitalized on the equilibrium

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(2) R. C. Petry and J. P. Freeman, J. Am. Chem. Soc., 83, 3912 (1961).

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dissociation of tetrafluorohydrazine into NF_2 free radicals[3], by generating

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(3) F. A. Johnson and C. B. Colburn, ibid., 83, 3043 (1961).

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t-butyl radicals via the decomposition of azoisobutane in the presence of

tetrafluorohydrazine. The synthesis of azoisobutane has been accomplished by two methods[4,5]. Using the more efficient of these methods[5], which in our

(4) E. Farenhorst and E. C. Kooyman, Rec. trav. chim., 72, 993 (1953).

(5) T. E. Stevens, J. Org. Chem., 26, 2531 (1961).

hands gave a 30% yield of the intermediate, the overall yield of t-butyldifluoramine obtained in the two-step reaction sequence was only 6% of theoretical.

Ethyl- and methyldifluoramine have been prepared by reaction of the respective iodides with tetrafluorohydrazine excited by ultraviolet radiation ($\geq$ 2750 Å).[6] We therefore investigated the free radical reaction of t-butyl

(6) J. W. Frazer, J. Inorg. Nucl. Chem., 16, 63 (1960).

iodide with tetrafluorohydrazine and found that it produced the desired t-butyldifluoramine routinely in 40% yield. The reaction is believed to take place by following steps:

$$2(CH_3)_3CI \longrightarrow 2(CH_3)_3C\cdot + I_2 \qquad (1)$$

$$N_2F_4 \rightleftharpoons 2NF_2\cdot \qquad (2)$$

$$(CH_3)_3C\cdot + NF_2\cdot \longrightarrow (CH_3)_3CNF_2 \qquad (3)$$

t-Butyldifluoramine was obtained by exposing a mixture of the reactants in Pyrex to light from a 300-watt Reflectorflood lamp for 20 hours or, more

conveniently, by heating to 100° for 4 hours. The yield of product in the thermal reaction was not increased by a 50% increase in reaction time.

The crude product was purified by trap-to-trap distillation in a vacuum system followed by fractional distillation at atmospheric pressure. It was identified by boiling point and elemental analysis. Its infrared spectrum and fragmentation pattern in the mass spectrometer were also consistent with the assigned structure.

The presence of small amounts of C_8 and C_{12} olefins (telomers of isobutene) among the reaction products attests to the occurrence of disproportionation between t-butyl radicals (equation 4). Coupling of t-butyl radicals (equation 5)

$$2(CH_3)_3C\cdot \longrightarrow (CH_3)_3CH + (CH_3)_2C{=}CH_2 \qquad (4)$$

also occurred to a minor extent, as evidenced by the appearance of traces of tetramethylbutane (equation 5).

$$2(CH_3)_3C\cdot \longrightarrow (CH_3)_3CC(CH_3)_3 \qquad (5)$$

EXPERIMENTAL

A 2-l. Pyrex bulb, fitted with a freeze-out tip and a vacuum stopcock terminating in a standard ball joint, was charged with 6.0 g. (0.033 mole) of t-butyl iodide[7] in a nitrogen atmosphere. The liquid was frozen at -78° and the bulb

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(7) Obtained from K and K Laboratories, Jamaica, N. Y., and distilled before use, b.p. 99-100°.

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was evacuated. After three additional freeze-thaw cycles with intermittent evacuation, the tip of the flask was cooled to -196° and 4.16 g. (0.040 mole, measured by volume assuming ideal gas properties) of tetrafluorohydrazine was condensed into the bulb. The bulb was then transferred to a heating jacket and heated to 95 ± 5° for 4 hr. Following this, the bulb was cooled to room temperature, the contents were condensed in the tip at -78°, and any volatile components were removed under vacuum. The crude t-butyldifluoramine was then distilled under vacuum from the bulb at 28° into a trap at -78°. This synthesis was repeated four times and the combined products were fractionated to yield 5.8 g. (40.7%) of colorless liquid, b.p. 55-56° (760 mm.).

The infrared spectrum showed very strong absorptions at 878 and 972 $cm.^{-1}$ and a weak band at 930 $cm.^{-1}$, indicative of NF_2 groups. The expected symmetrical and asymmetrical CH_3-C deformation bands (1480 and 1375 $cm.^{-1}$, respectively) and the C-H stretching band (2990 $cm.^{-1}$) were also observed. The mass spectrum, although lacking the molecule ion peak, did show the following significant fragements (m/e, assignment, relative intensity): 94, $C_3H_6NF_2^+$, 6.3; 57, $C_4H_9^+$, 100; 33, NF^+, 4.5

In the photolytic process, a 500-ml. Pyrex bulb containing 1.5 g. (8.2 mmoles) of t-butyl iodide and 1.58 g. (15.2 mmoles) of tetrafluorohydrazine

was illuminated with a 300-watt Reflectorflood lamp at a distance of 15 cm. for 24 hr. Upon working up the reaction mixture as described above, 0.4 g. of pure t-butyldifluoramine was obtained.

Acknowledgement - The authors wish to thank Dr. Donald D. Perry for his interest in and encouragement of this work. We are also indebted to Raymond N. Storey, Donald Y. Yee, and John Creatura for instrumental and elemental analyses.

III. APPENDIX - DIFLUORAMINE CHEMISTRY

A. DISCUSSION

In general, two factors are involved in the complete understanding of the chemical nature of a functional group. These factors are:

(1) The transformations of the functional group itself, involving either displacement in toto or disruption of the group by displacement of a component part.

(2) The influence of the group upon the reactivities of other functionalities in the same molecule.

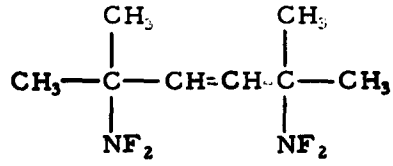
These two factors are not mutually exclusive, however, for the reactivity of a functional group is not constant. It varies in kind, as well as in degree, with changes in structure and functionality of the parent molecule. These general considerations have helped to mold this research program and single out specific areas for most fruitful experimental study.

The selection of specific topics for investigation from such a broad array of challenging possibilities is subject to pressures from two conflicting philosophies. It is obviously desirable, on the one hand, to acquire as much information as possible about the behavior of those compounds which are of greatest practical interest. In contrast to this approach, it can be argued that more intensive study of simpler model compounds will produce a more fundamental understanding of the chemistry of the difluoramino group, which can then be applied with greater generality. During the past year we have favored the latter approach.

1. Synthesis and Reactions of 1,4-bis(Difluoramino)cyclohexene-2

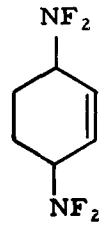
An understanding of the chemistry of difluoramino compounds necessarily includes a knowledge of the influences of difluoramino groups and other functional groups upon each other. The reactivity of a double bond adjacent to two NF_2 groups has been reported (Ref 1) to be very low when 2,5-bis(difluoramine)-2,5-dimethylhexene-3 (I) was used as a model compound. The double bond is

sterically crowded in I, however, and this may exert a greater influence than

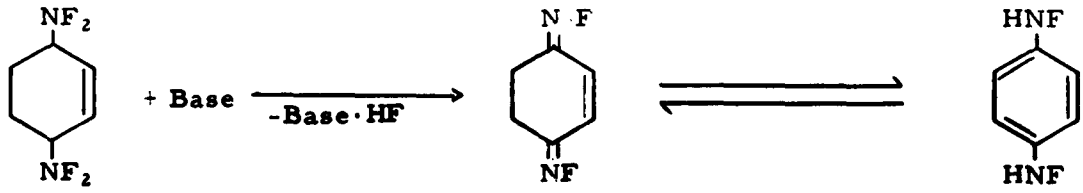


I

the electronic effect of the adjacent NF_2 groups. This steric requirement is greatly decreased in 1,4-bis(difluoramino)cyclohexene-2 (II) and the compound is, therefore, a good model for a study of this type. The oxidation of II, for



instance, might lead to the formation of 2,5-bis(difluoramino)adipic acid, a useful intermediate in the synthesis of NF_2 containing polymers. Dehydrofluorination of II should lead to a bis(fluorimino)compound which would be in tautomeric equilibrium with an aromatic NFH compound.



II (1)

The synthesis of II was accomplished by the addition of tetrafluorohydrazine to 1,3-cyclohexadiene. The thermally initiated reaction proceeded smoothly to give a 52 to 62% yield of 1,1 addition product, bp 65-66°C/15 mm (Table I). Elemental analysis and the infrared spectrum (Figure 1) indicated that the

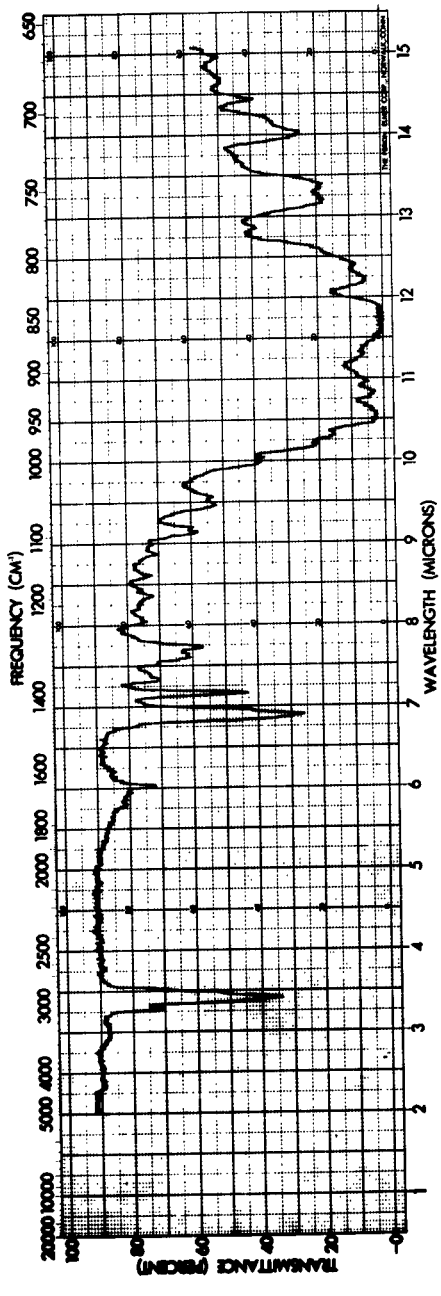


Figure 1. bis(Difluoramino)cyclohexene Isomers Mixture

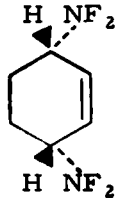
material was bis(difluoramino)cyclohexene. Gas chromatography revealed the presence of four components (Table II). The four possible structures are:

cis-,4-bis(difluoramino)cyclohexene-2 (II a)

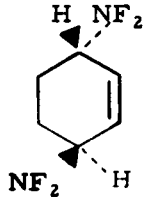
trans-1,4-bis(difluoramino)cyclohexene-2 (II b)

cis-1,2-bis(difluoramino)cyclohexene-3 (II c)

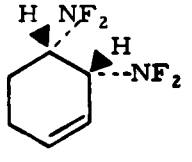
trans-1,2-bis(difluoramino)cyclohexene-3 (II d).



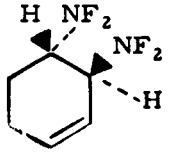
II a



II b



II c



II d

The components were separated by preparative scale gas chromatography and analyzed by infrared spectroscopy but no definite assignments could be made. The chromatographic separation will be repeated and the components identified by nuclear magnetic resonance. This information may give us some further insight into the steric course of the reaction, although it does appear at this time that 1,2 and 1,4 additions occurred at similar rates.

The dehydrofluorination of 1,2-bis(difluoramino)cyclohexane with ethanolic KOH was reported (Ref 1) to yield 1,2-bis(fluorimino)cyclohexane. As a first attempt to dehydrofluorinate the isomer mixture (II a-d), therefore, ethanolic KOH was used. The reaction was exothermic and the mixture became very dark. Distillation of the brown residue obtained after workup yielded a small amount of red liquid, bp 55-60°/0.2 mm, which did not have a well defined infrared spectrum, but appeared to contain N-F bonds. In addition, a black polymeric solid was obtained. Since this procedure did not appear to be synthetically useful, a milder dehydrofluorinating agent was sought.

An ether solution of II was stirred with pyridine at 30°C for 24 hours. The deep red solution was filtered and the residue obtained after evaporation of the solvent was distilled to give a 37% yield of pale yellow liquid, bp 41-42°C / 0.1 mm. This material exhibited infrared absorptions indicative of a fluorimino compound, but it turned brown after standing for two days at -5°C and could not be characterized.

TABLE I

REACTION OF 1,3-CYCLOHEXADIENE WITH N_2F_4

Diene gm (moles)	N_2F_4 (moles)	Time (hr)	Temp (°C)	Product gm (moles)	Yield[a] (%)
1.00 (0.0125)	0.015	3	80-100	1.77 (0.0096)	60.0
3.36 (0.0400)[b]	0.06	3	80-100	4.07 (0.0221)	52.5
8.0 (0.10)[c]	0.12	4	80-100	11.50 (0.0625)	62.5

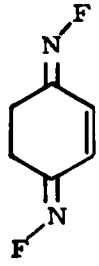
a. Based on the amount of 1,3-cyclohexadiene.
b. Combination of two runs.
c. Combination of four runs.

TABLE II

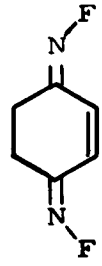
GAS CHROMATOGRAPHIC ANALYSIS
OF BIS(DIFLUORAMINO)CYCLOHEXENE

Peak No.	Retention Time (min)	Wt (%)
1	10.3	24.5
2	12.0	37.0
3	13.75	23.9
4	16.50	14.6

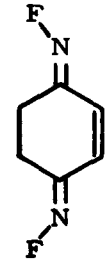
Anion exchange resins are often effective in the dehydrohalogenation of organic compounds. An ether solution of 1.84 gm of II was therefore stirred with four molar equivalents of Amberlite IR-45, a weakly basic anion exchange resin, for four hours at room temperature. After the blackened resin was filtered off, the deep red solution was stripped of solvent to yield 1.0 gm of brown oil. The infrared spectrum of this oil was similar to that obtained from the product of the pyridine reaction. The material was crystallized from pentane to yield a small amount of colorless crystals, mp 50-51°C. An overall yield of 11.3%, based on cyclohexadiene, was obtained. Elemental analysis of the solid was in excellent agreement with theory for bis(fluorimino)cyclohexene. The infrared spectrum (Figure 2) showed strong absorption in the N-F region, as well as sharp peaks at 1580, 1610 and 1630 cm^{-1} indicative of C=N or C=C absorptions. The ultraviolet spectrum showed a strong, broad absorption with a maximum at 239 millimicrons ($\epsilon \cong 10^{5}$). On the basis of these facts, the structure of 1,4-bis(fluorimino)cyclohexene-2 was assigned to the material. This was confirmed by the proton magnetic resonance spectrum (Figure 3) which consisted of two sharp intense singlets at 174 and 397 $\pm$ cps downfield from tetramethylsilane. The relative intensities of the two bands were not measured but they appeared to be close to the expected 2:1 ratio; the more intense peaks occurred at higher field strength. Each singlet is superimposed on a complex system, suggesting that a mixture of isomers is present. Three geometric isomers of 1,4-bis(fluorimino)cyclohexene-2 are possible: syn-anti (III a), syn-syn (III b), anti-anti (III c). Gas chromatography of the material



III a



III b



III c

did indeed indicate the presence of two components. These will be separated by preparative scale gas chromatography in an effort to collect and identify the individual isomers.

In an attempt to tautomerize III, a small sample was heated at 110 to 120°C for 20 hours, but no change in melting point or infrared spectrum was

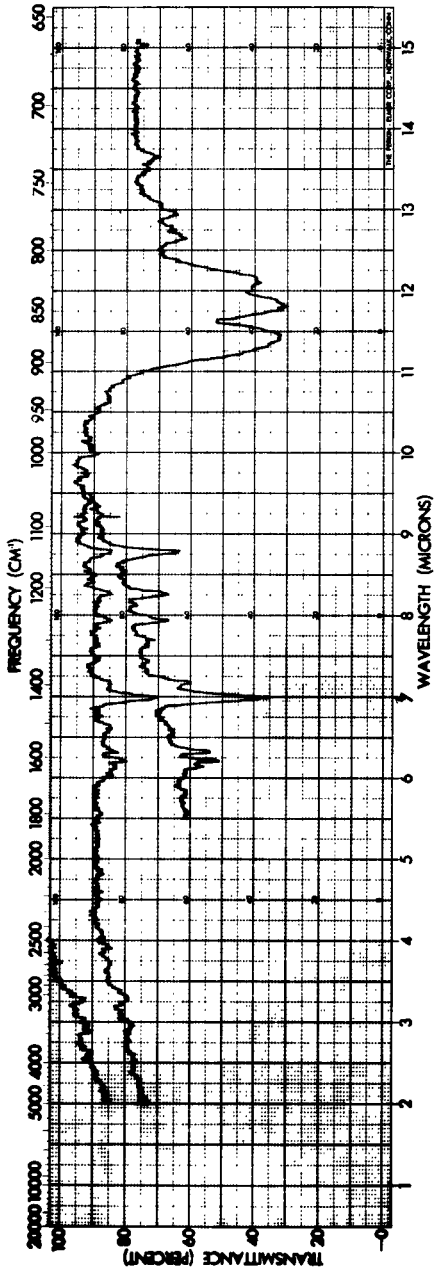


Figure 2. 1,4-bis(Fluoramino)cyclohexene

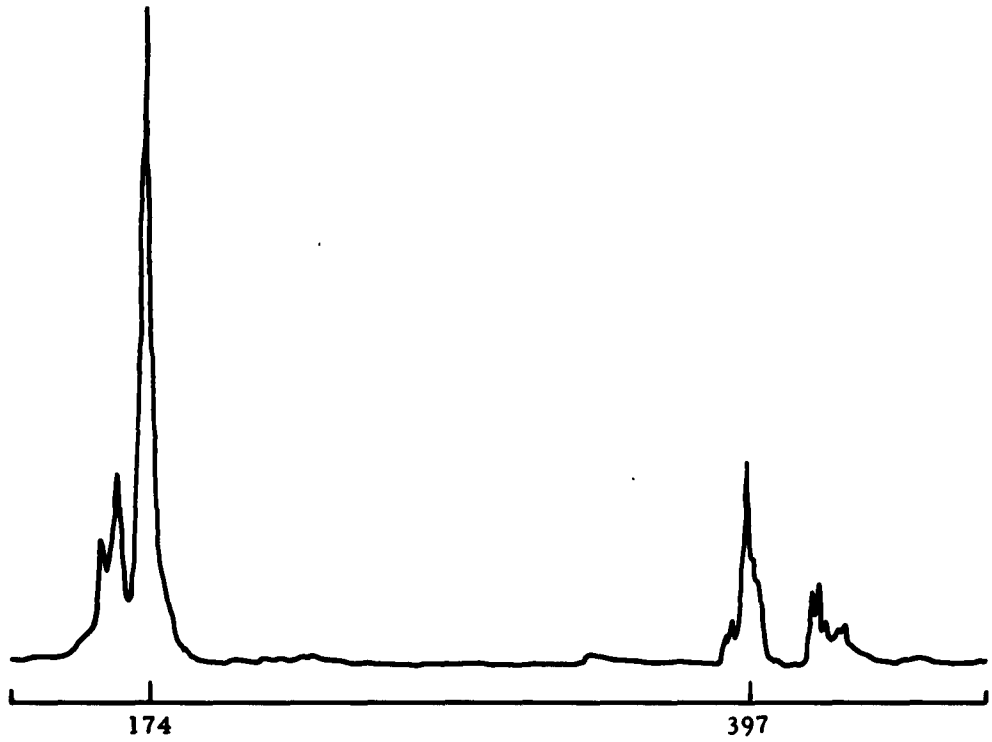


Figure 3. Proton Resonance of 1, 4-bis(Fluorimino)cyclohexane-2

In anticipation of an extension of the oxidation studies to acidic media, the stability of trityldifluoramine in various acids is being investigated. It is known (Ref 7) that this compound reacts with sulfuric acid to liberate difluoramine.

$$\phi_3CNF_2 + H_2SO_4 \longrightarrow HNF_2 + \phi_3C^+ + HSO_4^- \qquad (5)$$

A small amount of trityldifluoramine was mixed with glacial acetic acid at room temperature. It dissolved completely without the evolution of gas or other indication of reaction. Upon dilution with water, a finely divided white precipitate appeared; upon standing at room temperature, the solid digested to yield a filterable crystalline product. The crystals darkened (dull green color) on standing but the infrared spectrum showed only those absorptions associated with trityldifluoramine.

B. EXPERIMENTAL

1. Addition of Tetrafluorohydrazine to 1,3-Cyclohexadiene

A 2-liter Pyrex bulb was charged with 1.0 gm (12 mmoles) of 1,3-cyclohexadiene under a stream of nitrogen. The liquid was cooled to -78°C and the bulb evacuated. After degassing several times, 15 mmoles of N_2F_4 (tetrafluorohydrazine) was condensed at -196°C and the bulb heated at 80 to 100°C for 3 hours. At the end of this time, practically all of the N_2F_4 had been consumed and the liquid was distilled from the bulb into a -78°C trap. The crude product, 1.77 gm, was redistilled to yield 1.38 gm (60%) bis(difluoramino) cyclohexene isomer mixture, bp 65-68°C/12.5 mm.

Anal. Calcd for $C_6H_8N_2F_4$: C, 39.14; H, 4.38; N, 15.21; F, 41.27

Found: C, 38.84; H, 4.42; N, 15.26; F, 41.48 (by diff).

The product was chromatographed with the Aerograph A-90-P using a 5-foot column containing 20% SF 96 silicone oil on firebrick. The operating conditions of the instrument are as follows:

Injector temp:	180°C	Attenuation:	1 X
Column temp	115°C	Sample size:	1 microliter
Detector temp:	225°C	He flowrate:	59 ml/min

The area under each peak was measured with a planimeter.

2. Dehydrofluorination of bis(Difluoramino)cyclohexene Isomers

a. KOH in Ethanol

A solution of 1.84 gm (10 mmoles) of the bis(difluoramino)cyclohexene isomer mixture in 10 ml of absolute ethanol was added dropwise to a solution of 1.12 gm (20 mmoles) KOH in 25 ml of ethanol at 0 to 5°C over a period of one hour. The brown mixture was allowed to warm and was stirred at room temperature for one hour. The mixture was then filtered, the solvent was removed from the filtrate, and the residue was distilled to yield 0.35 gm of red liquid, bp 55-60°C/0.2mm. The distilling flask contained 0.2 gm of black polymeric material.

b. Pyridine

A solution of 1.58 gm (20 mmoles) of pyridine and 1.84 gm (10 mmoles) of the bis(difluoramino)cyclohexene isomer mixture in 35 ml of diethylether was stirred at 30°C for 24 hours. The dark solid which precipitated was filtered off and the ether solution evaporated to dryness. The residual brown oil was distilled to give 0.53 gm of pale yellow liquid, bp 41-2°C/0.1 mm, mp 17-18°C. The liquid turned dark brown upon standing for two days at -5°C.

c. Ion Exchange Resin

A solution of 1.84 gm (10 mmoles) of the bis(difluoramino)cyclohexene isomer mixture in 20 ml ether was stirred with 8.0 gm (40 mmoles) of weakly basic ion exchange resin (Amberlite IR-45, 5.0 meq/gm) for four hours at room temperature. The solution became deep red and the resin turned black. The resin was filtered off and washed with ether. The solvent was evaporated from the combined filtrate and washed, leaving 1.0 gm of brown oil, which was crystallized from pentane to yield 0.15 gm (10.5%) of colorless crystals, mp 50-1°C.

Anal. Calcd for $C_6H_6N_2F_2$: C, 50.00; H, 4.20; N, 19.44; F, 26.36

Found: C, 49.89; H, 4.31; N, 19.45; F, 26.40.

The ultraviolet spectrum was recorded with a Beckman DK-2 spectrophotometer. The maximum absorption occurred at 239 millimicrons with an extinction of approximately 10^5.

The proton resonance spectrum was recorded with a Varian Associates DP-60 spectrometer. The sample was prepared in $CFCl_3$ solution containing 1 to 2% tetramethylsilane as an internal reference.

The product was chromatographed with an Aerograph A-90-P, using a 5-foot column containing 20% SF 96 silicone oil or firebrick. The operating condition of the instrument was as follows:

Injector temp :	180°C	Attenuation:	1 X
Column temp :	160°C	Single size:	2 ml of 50% solution
Detector temp:	260°C	He flowrate:	50 ml/min in $CH \cdot Cl_2$

Under these conditions peaks appeared at 10.75 and 13.5 minutes retention time relative to air.

C. REFERENCES

1. Report RMD 076-S-61, Difluoramine Chemistry, Thiokol Chemical Corporation, Reaction Motors Division, 1 December 1961.

2. Report RMD 076-S-62, Difluoramine Chemistry, Thiokol Chemical Corporation, Reaction Motors Division, 31 December 1962.

3. Report RMD-AOR-Q1-63 (Section I), "Difluoramine Chemistry," Advanced Oxidizer Research, Thiokol Chemical Corporation, Reaction Motors Division, 30 April 1963.

4. Report RMD-AOR-Q2-63 (Section I), "Difluoramine Chemistry," Advanced Oxidizer Research, Thiokol Chemical Corporation, Reaction Motors Division, 31 July 1963.

5. Report RMD-AOR-Q3-63 (Section I), "Difluoramine Chemistry," Advanced Oxidizer Research, Thiokol Chemical Corporation, Reaction Motors Division, 31 October 1963.

6. Report R-3070-1, Rocketdyne, 25 August 1961.

7. W. H. Graham and C. O. Parker, J. Org. Chem. 28, 850 (1963).

Section II

RMD Project 5007

(U)
SYNTHESIS OF COMPOUNDS FOR STRUCTURE-SENSITIVITY STUDY

CONFIDENTIAL

Thiokol
REACTION MOTORS DIVISION

Section II

SYNTHESIS OF COMPOUNDS FOR STRUCTURE-SENSITIVITY STUDY

A. P. Kotloby
D. D. Perry

Report RMD AOR-ATS-63

RMD Project 5007
Report Period: 1 January 1963 to
31 December 1963

Contract No. NOnr 3664(00)
ARPA Order No. 23
Project Code 3910

CONFIDENTIAL

This report has been distributed in accordance with a combined LPIA-SPIA Distribution List in effect as of the publication date of this report.

FOREWORD

This annual summary report was prepared by Thiokol Chemical Corporation, Reaction Motors Division, Denville, New Jersey, under Contract No. NOnr 3664(00), ARPA Order No. 23. The research reported herein was administered under the direction of the Power Branch, Office of Naval Research, with Mr. R. L. Hanson as Project Engineer.

This report covers work conducted during the period of 1 January 1963 to 31 December 1963 on RMD Project 5007.

The following personnel participated in this research: A. P. Kotloby (Project Scientist); W. H. Wieting and J. R. Crothamel (Synthesis); R. N. Storey, D. G. Chowanec, J. A. Creatura, and D. N. Pregler (Instrumental and Wet Chemical Analysis).

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ILLUSTRATIONS

TABLES

ABSTRACT

Work is reported on the synthesis of a series of aliphatic difluoramines containing both vicinal and geminal NF_2 groups for the evaluation of relationships between structure and sensitivity. In addition to difluoraminoalkanes and cycloalkanes, a number of organofunctional difluoramines were prepared in order to evaluate the effect of various substituent groups on sensitivity. The compounds prepared were principally liquids or low-melting solids, having a C/NF_2 ratio of 3:1 or less. The following types of compounds were prepared during the period covered by this report:

1. Vicinal and geminal bis(difluoramino)cycloalkanes and normal and branched-chain bis(difluoramino)alkanes.

2. Mixed vicinal - geminal tetrakis(difluoramino)alkanes.

3. Vicinal bis(difluoramino)-n-alkenes, cycloalkenes, perfluoroalkanes, ketones, acids, alcohols, esters, and nitriles.

Purified samples of these compounds were sent to the Naval Ordnance Laboratory for sensitivity testing.

I INTRODUCTION

Investigations in the field of NF chemistry have opened several routes to the synthesis of poly(difluoramino) organic compounds. Much effort is being made to utilize the inherent energy of organodifluoramines in propellant compositions. A common feature of these compounds is their sensitivity to impact and other external stimuli. Since propellants are subjected to various kinds of stresses during manufacture, storage and use, the study of the impact and thermal sensitivity of organodifluoramines is important in assessing their practical value as propellants.

In order to determine whether systematic relationships between the structure and sensitivity of this class of compounds can be established, the Reaction Motors Division of Thiokol Chemical Corporation has undertaken a cooperative program with the Naval Ordnance Laboratory, White Oak, Maryland, for the preparation and sensitivity evaluation of a series of organic difluoramines. The preparation and purification of the compounds is the responsibility of Reaction Motors Division, while sensitivity tests are conducted at the Naval Ordnance Laboratory.

Initial efforts on this program were directed toward the synthesis of vicinal bis(difluoramino)alkyl carbamates and dicarbamates (Ref 1) since these compounds were expected to be solids, were stable above their melting points, and could be evaluated by both the thermal explosion delay test (Ref 2) and the Bureau of Mines-type dropweight test (Ref 3) However, the carbamate group is a low energy group and only a limited number of carbamates were sufficiently sensitive to give meaningful results in the thermal explosion delay test. Since the latter test has now become of much greater interest because of refinements which have improved its accuracy, the need for solid compounds has diminished, and work during the past year has reemphasized the preparation of difluoramines which do not contain the carbamate group.

The overall objective of the program is to obtain a correlation of the effect of the structural characteristics of the difluoramines, such as vicinal vs geminal substitution, oxidative balance, nature of functional groups, etc., with sensitivity. Sensitivity results on many of these compounds have been reported separately (Ref 4.)

II. MANUSCRIPT OF PAPER FOR PUBLICATION

The Synthesis of a Series of Organic Difluoramines

Prepared for Submission to the
Journal of Organic Chemistry

Thiokol
REACTION MOTORS DIVISION

[Contribution from the Chemistry Department, Reaction Motors Division, Thiokol Chemical Corporation, Denville, N.J.]

The Synthesis of a Series of Organic Difluoramines[1]

Prepared by Anatole P. Kotloby and Donald D. Perry

(1) This work was supported by the Advanced Research Project Agency under Contract NOnr 3664(00), ARPA Order No. 23.

A series of organic difluoramines, consisting of vicinal, 1,4-, and geminal bis(difluoramino) derivates, has been prepared by the reaction of N_2F_4 with the appropriate olefinic compounds and by the reaction of difluoramine with aldehydes or ketones in fuming sulfuric acid. The methods of preparation and purification, together with pertinent properties of the synthesized compounds, are described.

Introduction

Organic compounds containing the difluoramino group are of considerable interest as potential explosives and propellants. In common with other compounds containing strong oxidizing groups, they are often characterized by instability and shock sensitivity. In order to develop an understanding of the structural factors affecting sensitivity in the organic difluoramine series, a

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program was initiated to evaluate the sensitivity of a large number of difluoramines having a variety of structural features. The present paper describes the synthesis of a group of vicinally and geminally substituted difluoramines for this study. The methods of synthesis are essentially those that have been described by earlier workers,[2,3] with some minor modifications which were

(2) Rohm and Haas Co., Report No. P-58-18, Quarterly Progress Report on Synthetic Chemistry, Part II. Organic Chemistry, October 1958, inter alia.

(3) Ibid, Report No. P-61-24, February 1961, Aerojet-General Corporation, Special Report on Contract NOnr 2655(00), March 1, 1961.

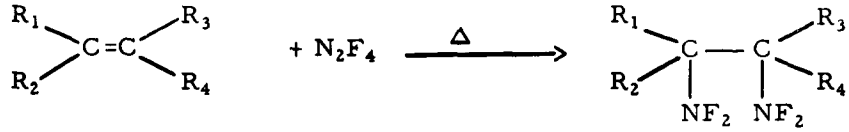
necessitated by the characteristics of individual starting materials. Since the compounds prepared covered a wide range of aliphatic and alicyclic difluoramines and included some types of organofunctional difluoramines not previously described, it was believed that publication of data on their preparation and physical properties would be of interest at this time. Sensitivity data obtained on these compounds will be reported elsewhere.

Experimental

Reagents. - Organic reagents were obtained from various commercial sources and were distilled prior to use. Dinitrogen tetrafluoride (technical grade) was

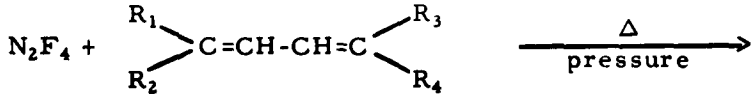
obtained from Air Products and Chemicals, Inc., Allentown, Pennsylvania and used without further purification

1,2- and 1,4-Bis(difluoramines). - The vicinal bis(difluoramines) were prepared by the reaction of N_2F_4 with compounds containing a single nonconjugated double bond (equation 1).

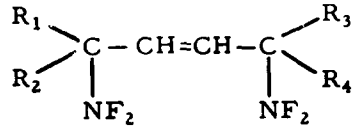


(1)

The two examples of 1,4-bis(difluoramines) (Table I) were obtained as the major products from the addition of N_2F_4 to conjugated dienes (equation 2).



(2)



(mixture of isomers)

The olefin (0.04 mole), dissolved in Freon-113 (15 ml.), and dinitrogen tetrafluoride (0.05 mole) were heated overnight at 80° in a stainless steel Hoke cylinder at an initial pressure of 280 p.s.i.g. The reaction mixture was then cooled to -80° and the unreacted N_2F_4 removed on a vacuum line. The product was then freed of solvent and distilled under reduced pressure. The

vicinal bis(difluoramino)alkanes and cycloalkanes prepared, together with pertinent data on reaction conditions, yields, elemental analyses, and physical properties, are listed in Table I. Data on vicinal and 1,4-bis(difluoramines) containing functional groups are listed in Table II.

gem-Bis(difluoramines).- The gem-bis(difluoramines) were prepared by the reaction of an aldehyde or ketone with difluoramine (HNF_2) in fuming sulfuric acid (equation 3).[3] Difluoramine for these reactions was prepared by the method

$$R_1\text{-}\underset{\underset{O}{\|}}{C}\text{-}R_2 + 2HNF_2 \xrightarrow{H_2SO_4 - SO_3} R_1\text{—}\overset{\overset{NF_2}{|}}{\underset{\underset{NF_2}{|}}{C}}\text{—}R_2 + H_2O \qquad (3)$$

of Lawton and Weber[4]. Details of the preparation as carried out in our work are given below.

(4) E. A. Lawton and J. Q. Weber, J. Am. Chem. Soc., 85, 3595 (1963).

Difluoramine.- A 1000-ml. three-neck flask, equipped with a magnetic stirrer, was filled with a solution of 50 g. (0.83 mole) of urea dissolved in 600 ml. of water. The solution was cooled to 0° by means of an ice-water bath. A 20% (by volume) mixture of fluorine and nitrogen was bubbled through the vigorously stirred solution while the temperature was kept at 0-5°. Over a period of 6 hr., a total of 2.0 moles of fluorine was bubbled through the solution. The solution was then stirred for an additional hour under a stream of nitrogen.

Table I

Geminal Bis(Difluoramines)

Name	Yield %	M.p. °C	B.p. °C/mm Hg	B.p. °C/760mm Hg	n_D^{25}
., 1-Bis(difluoramino)propane	18	-	31.0/160	74	
1, 1-Bis(difluoramino)butane	20	-	46.0/116	95	1.3611
2, 2-Bis(difluoramino)butane	31	-	42.0/85	102	1.3578
2, 2-Bis(difluoramino)pentane	63	-	44.0/40	121	1.3701
3, 3-Bis(difluoramino)pentane	51	-	51.0/49	122	1.3770
2, 2-Bis(difluoramino)-4-methylpentane	54	-	54.5/38	137	1.3792
1, 1-Bis(difluoramino)hexane	65	-	52.5/25	140	1.3740
2, 2-Bis(difluoramino)hexane	80	-	56.0/30	145	1.3748
3, 3-Bis(difluoramino)hexane	33	-	56.5/28	147	1.3845
1, 1-Bis(difluoramino)cyclopentane	81		60.0/60	-	-
1, 1-Bis(difluoramino)cyclohexane	50	-	50.0/10	-	1.4080
2, 2-Bis(difluoramino)-3, 3-dimethylbutane	22	89.0-90.0	-	-	-
1, 2, 5, 5-Tetrakis(difluoramino)hexane	96	-	48.0/0.32	207	1.3866
				Vicinal Bis(Difluoramines)	
1, 2-Bis(difluoramino)ethane	76	-	36.0/180	70	1.3297
1, 2-Bis(difluoramino)-3, 3-dimethylbutane	65	-	62.0/45	144	1.3821
2, 3-Bis(difluoramino)-2, 3-dimethylbutane	73	64.0-66.0	-	-	-
1, 2-Bis(difluoramino)pentane	71	-	53.0/50	129	1.3686
2, 3-Bis(difluoramino)pentane	80	-	46.0/38	122	1.3715
1, 2-Bis(difluoramino)-2-methylpentane	74	-	52.5/26	144	1.3824
1, 2-Bis(difluoramino)-3-methylpentane	60	-	55.0/26	147	1.3812
2, 3-Bis(difluoramino)-2-methylpentane	79	-	55.0/36	141	1.5065
1, 2-Bis(difluoramino)hexane	84	-	58.0/30	144	1.3770
1, 2-Bis(difluoramino)cyclopentane	54	-	47.0/40	150	1.3937
1, 2-Bis(difluoramino)cyclohexane	45	-	40.0/5	-	1.4123

Table I

Geminal Bis(Difluoramines)

B.p. °C/mm Hg	B.p. °C/760mm Hg	n_D^{25}	Formula	C, % Calcd.	C, % Found.	H, % Calcd.	H, % Found	N, % Calcd.	N, % Found
31.0/160	74		$C_3F_4H_6N_2$	24.67	24.95	4.14	4.27	19.18	18.73
46.0/116	95	1.3611	$C_4F_4H_8N_2$	30.01	30.01	5.04	5.54	17.50	17.55
42.0/85	102	1.3578	$C_4F_4H_8N_2$	30.01	30.00	5.04	5.71	17.50	17.16
44.0/40	121	1.3701	$C_5F_4H_{10}N_2$	34.49	35.50	5.79	6.22	16.09	15.93
51.0/49	122	1.3770	$C_5F_4H_{10}N_2$	34.49	34.72	5.79	6.04	16.09	16.63
64.5/38	137	1.3792	$C_6F_4H_{12}N_2$	38.30	38.06	6.43	6.13	14.89	14.53
62.5/25	140	1.3740	$C_6F_4H_{12}N_2$	38.30	37.94	6.43	6.42	14.89	14.57
66.0/30	145	1.3748	$C_6F_4H_{12}N_2$	38.30	38.79	6.43	7.13	14.89	13.84
66.5/28	147	1.3845	$C_6F_4H_{12}N_2$	38.30	38.49	6.43	6.60	14.89	15.10
60.0/60	-	-	$C_5F_4H_8N_2$	34.89	34.66	4.68	4.47	16.17	15.82
60.0/10	-	1.4080	$C_6F_4H_{10}N_2$	38.71	39.02	5.41	4.48	15.05	15.18
-	-	-	$C_6F_4H_{12}N_2$	38.30	38.53	6.43	6.62	14.89	13.93
48.0/0.32	207	1.3866	$C_6F_8H_{10}N_4$	24.84	25.04	3.47	3.99	19.31	20.51

Vicinal Bis(Difluoramines)

36.0/180	70	1.3297	$C_3F_4H_4N_2$	18.19	18.22	3.05	3.26	21.21	21.45
62.0/45	144	1.3821	$C_6F_4H_{12}N_2$	38.30	38.13	6.43	6.57	14.89	14.81
-	-	-	$C_6F_4H_{12}N_2$	38.30	36.91	6.43	6.60	14.89	14.06
53.0/50	129	1.3686	$C_5F_4H_{10}N_2$	34.49	34.98	5.79	5.45	16.09	15.94
46.0/38	122	1.3715	$C_5F_4H_{10}N_2$	34.49	34.41	5.79	5.91	16.09	16.10
52.5/26	144	1.3824	$C_6F_4H_{12}N_2$	38.30	38.50	6.43	6.65	14.89	15.16
55.0/26	147	1.3812	$C_6F_4H_{12}N_2$	38.30	38.96	6.43	7.36	14.89	15.36
55.0/36	141	1.5065	$C_6F_4H_{12}N_2$	38.30	37.60	6.43	7.09	14.89	14.76
58.0/30	144	1.3770	$C_6F_4H_{12}N_2$	38.30	38.42	6.43	6.40	14.89	14.48
47.0/40	150	1.3937	$C_5F_4H_8N_2$	34.89	34.76	4.68	4.83	16.27	16.16
40.0/5	-	1.4123	$C_6F_4H_{10}N_2$	38.71	38.00	5.41	4.48	15.05	14.60

Table II

Functional Organodifluoramines

Name	Yield %	B.p. °C/mm Hg	B.p. °C/760 mm Hg	n_D^{25}	Formula
1,2-Bis(difluoramino)-5-hexanone	68	75.0/10	190d	1.3988	$C_6F_4H_{10}N$
3,4-Bis(difluoramino)butyronitrile	40	45.0/8	198	1.3924	$C_4F_4H_5N$
2,3-Bis(difluoramino)perfluorobutane	100	-	63	-	$C_4F_{12}N_2$
2,3-Bis(difluoramino)-2-methylpropionitrile	67	50.0/17	146	1.3690	$C_4F_4H_5N$
1-Methyl-1,2-bis(difluoramino)ethyl acetate	81	63.5/24	160	1.3767	$C_5F_4H_8N$
Ethyl 2,3-bis(difluoramino)butyrate	85	50.0/6	167	1.3870	$C_6F_4H_{10}$
1,2-Bis(difluoramino)ethyl propionate	82	65.0/28	160	1.3695	$C_5F_4H_8N$
1,2-Bis(difluoramino)ethyl butyrate	88	53.0/7.5	177	1.3759	$C_6F_4H_{10}$
4,5-Bis(difluoramino)pentanoic acid	74	99.0/0.4	215d	1.4400	$C_5F_4H_8N$
2,5-Bis(difluoramino)-2,5-dimethyl-Δ-3-furan	39	40.5/9	156	1.3975	$C_6F_4H_8N$
1,4-Bis(difluoramino)-2,3-dimethylbutene-2	45	55.0/9	157d	1.4400	$C_6F_4H_{10}$

Purity was determined by infrared spectrum and mass spectrum analysis.

Table II

Functional Organodifluoramines

mm Hg	B.p. °C, 760 mm Hg	n_D^{25}	Formula	C, % Calcd.	C, % Found	H, % Calcd.	H, % Found	N, % Calcd.	N, % Found
0	100d	1.3988	$C_6F_4H_{10}N_2O$	35.65	35.84	4.99	5.02	13.86	14.05
	105	1.3924	$C_4F_4H_5N_3$	28.08	27.48	2.95	2.44	24.56	24.74
	[illegible]	-	$C_4F_{12}N_2$*	-	-	-	-	-	-
7	146	1.3690	$C_4F_4H_5N_3$	28.08	27.64	2.95	3.17	24.56	24.60
4	166	1.3767	$C_5F_4H_8N_2O_2$	29.42	29.75	3.95	4.03	13.72	13.78
	167	1.3870	$C_6F_4H_{10}N_2O_2$	33.04	32.91	4.62	5.04	12.84	13.12
8	168	1.3695	$C_5F_4H_8N_2O_2$	29.42	29.70	3.95	4.59	13.72	13.53
.5	177	1.3759	$C_6F_4H_{10}N_2O_2$	33.04	33.44	4.62	5.19	12.84	12.98
.4	215d	1.4400	$C_5F_4H_8N_2O_2$	29.42	29.68	3.95	3.88	13.72	14.03
	151	1.3975	$C_6F_4H_8N_2O$	36.01	35.74	4.03	4.66	14.00	13.89
	157d	1.4400	$C_6F_4H_{10}N_2$	38.71	38.71	5.41	5.52	15.05	15.05

nalysis.

The total volume of solution at the end of the reaction was 670 ml. Iodometric titration of the solution showed the presence of 4.0 meq./ml. of N,N-difluorourea, indicating a yield of 65 g. (70%). In order to avoid the detrimental effect of glass on the aqueous N,N-difluorourea, the solution was stored in polyethylene containers[5] at 0-5° until used. Difluoramine was generated from this solution,

(5) Rohm and Haas Co., Quarterly Progress Report No. P-63-2, 1963.

as required, by hydrolysis in the presence of H_2SO_4. The HNF_2 was then passed into a reactor containing a CH_2Cl_2 solution of a carbonyl compound to which was added conc. H_2SO_4. The difluoramine generator is shown in Fig. 1.

Reaction of Carbonyl Compounds with HNF_2. - The aldehyde or ketone (0.01 mole) was dissolved in 5 ml. of dichloromethane and the solution slowly added to a stirred mixture of 15 ml. of concentrated H_2SO_4, containing 4-6% SO_3, and 0.02 mole of difluoramine maintained under reflux with a Dry Ice condenser. After addition of the organic reagent was complete, the reactants were stirred for three more hours. At the end of this period, the -80° condenser had come to room temperature due to gradual evaporation of the Dry Ice. The reaction mixture was then extracted with dichloromethane and the organic layer washed with aqueous bicarbonate, with water until it was neutral, and dried over anhydrous $MgSO_4$. The filtered solution was freed of the solvent by evaporation and the residue was distilled

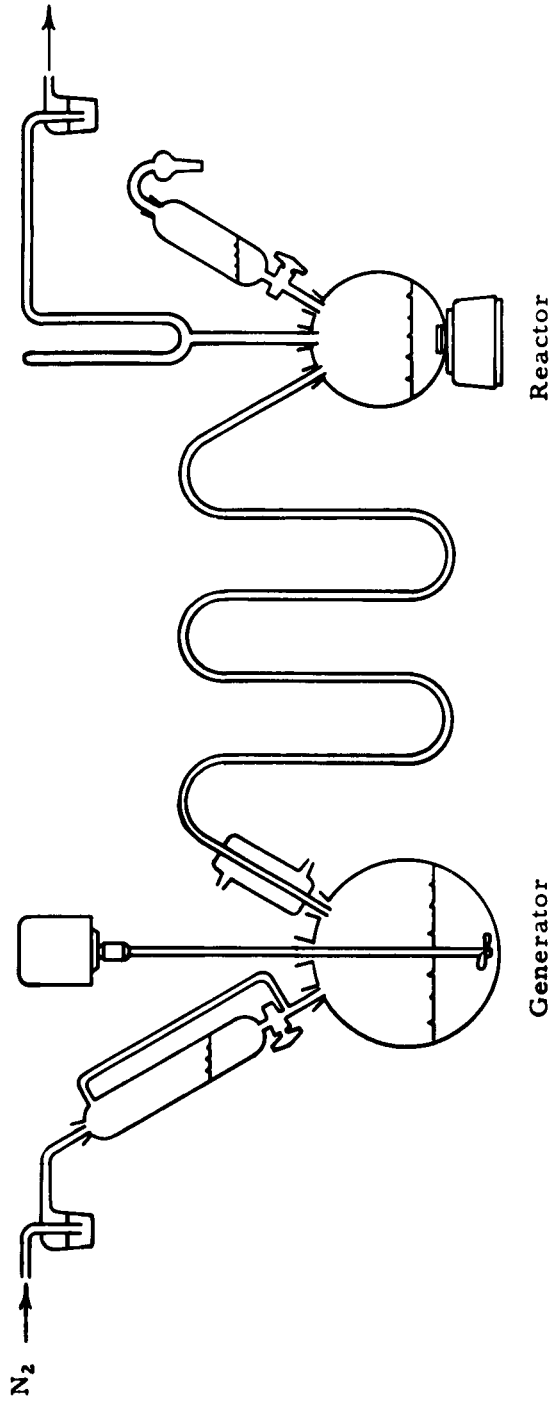


Figure 1. HNF_2 Generator and Reactor

from Aroclor 1242[6] (b.p. 325-366°) under reduced pressure. The gem-

(6) Obtained from Monsanto Chemical Co., Organic Chemicals Division, St. Louis, Missouri

bis(difluoramino) compounds have a sweet-pungent odor and are moderately impact-sensitive colorless liquids. Data on yields, physical constants and chemical analyses are summarized in Table I.

Acknowledgment. - The authors wish to thank Mr. W. H. Wieting for able assistance on the syntheses and Messrs. R. N. Storey, J. A. Creatura, D. N. Pregler and D. G. Chowanec for the infrared and chemical analyses.

III. APPENDIX - SYNTHESIS OF COMPOUNDS FOR STRUCTURE-SENSITIVITY EVALUATION

A. DISCUSSION

The synthesis phase of this research program was concerned with the selection, preparation, purification and characterization of a series of organo-difluoramines. Samples of these compounds were then submitted to the Naval Ordnance Laboratory for sensitivity evaluation. The selection of compounds was based primarily on the following considerations:

- Value of compound in providing information relating structure with sensitivity
- Synthesis feasibility
- Availability of candidate compounds from other sources.

In order to satisfy the first requirement several homologous series of compounds were synthesized. This permits evaluation of the effect of oxidative balance within a given series and of the effect of structural variations between corresponding members of different series. Thus, compounds having the general formula $CH_3(CH_2)_nCH(NF_2)CH_2NF_2$ (where, n = 0, 1, 2, or 3) have been prepared, as have the comparable compounds with the general formula $CH_3(CH_2)_nC(NF_2)_2R$ (where, R = -H, $-CH_3$, $-C_2H_5$). Comparison of sensitivity results within these two series can reveal effects due to oxidative balance, while comparison between corresponding members of different series provides information on the effect of vicinal and geminal substitution, isomerism, and other structural factors on sensitivity.

Compounds prepared to date have been vicinal bis(difluoramino)carbamates, tetrakis(difluoramino)dicarbamates, vicinal bis- and tetrakis(difluoramino)-alkanes and their derivatives, and geminal bis(difluoramino)alkanes. The preparation of fully characterized compounds has been described in Section II of this report. In this section work in progress and results not believed to be of publishable quality are summarized.

1. Synthesis of Vicinal Difluoraminoalkanes

The difluoraminoalkanes were prepared by the addition of tetrafluorohydrazine to olefins (equation 1). The types of compounds prepared included

$$RCH{=}CHR' + N_2F_4 \xrightarrow{\Delta} \overset{NF_2}{\underset{|}{R}}CH\text{---}\overset{NF_2}{\underset{|}{C}}HR' \qquad (1)$$

both saturated aliphatic difluoramines having branched structures and organofunctional derivatives containing a double bond, a nitrile, hydroxyl, carboxy, and an ester group. The completely characterized compounds prepared in 1963 by the N_2F_4 addition reaction were listed in Tables I and II, together with pertinent data on yields and properties.

2. Synthesis of Geminal Difluoraminoalkanes

The geminal derivatives were prepared by the reaction of difluoramine with the carbonyl compound in fuming H_2SO_4 (equation 2).

$$\overset{O}{\underset{||}{R}}CR' + 2HNF_2 \xrightarrow{H_2SO_4 + SO_3} \overset{NF_2}{\underset{NF_2}{\overset{|}{\underset{|}{R}}C}}R' + HOH \qquad (2)$$

where R = alkyl
R' = alkyl or H

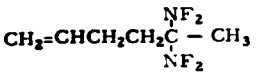
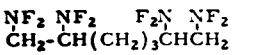
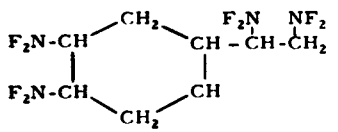
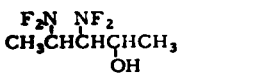
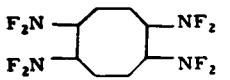
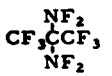
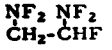
In the course of our work there were instances where the synthesis of particular NF_2 derivatives was complicated either because of the instability of the reaction product or because of the detrimental effect of side reactions. Since no individual compound was deemed to be absolutely essential for this project, little time was devoted to a thorough evaluation of the reaction conditions favoring the formation of the desired product. In some cases the product consisted of a mixture of compounds that could not be readily purified. Because of the incomplete status of this work, it could not be included in the Manuscript portion of this report (Section II). A list of these compounds, together with pertinent remarks, is given in Table III.

3. Synthesis of 1,1,1-Tris(difluoramino) Derivatives

During the last quarter of 1963 our efforts were directed toward the synthesis of compounds derived from perfluoroguanidine. This area will comprise a major portion of the synthesis effort during 1964. The workwill

Table III

List of Unfinished NF_2-Adducts

Compound	Experimental Conditions	Remarks
	HNF_2 addition to 1-hexene-5-one in the presence of 104%-H_2SO_4 at atmospheric pressure in CH_2Cl_2 solvent	Starting material was degraded. Most of HNF_2 recovered.
	N_2F_4 addition to 1,4-dichlorobutene-2 at 80° under 300 psig	The NF_2-adduct was readily obtained in a good yield but decomposed in storage to give HCl and other unidentified products.
	N_2F_4 addition to 1-6-heptadiene at 80° and an initial pressure of 420 psig	Reaction mixture detonated during warm-up period. Repeat of the reaction at lower temperature resulted apparently in the ring formation.
	N_2F_4 addition to vinyl-cyclohexene-4	A mixture of tetra- and two di- substituted derivatives was obtained, which requires further purification and identification.
	N_2F_4 addition to 3-pentene-2-ol at 80° in a pressure reactor	Most of the N_2F_4 was consumed, but the reaction product underwent dehydrofluorination and partial polymerization.
	N_2F_4 addition to 1,5-cyclooctadiene at 80° in a pressure reactor	A mixture of NF_2-adducts was formed. It requires further purification and identification.
	HNF_2 reaction with hexafluoroacetone in the presence of 104%-H_2SO_4 at -5 to -10° at atmospheric pressure	No reaction.
	N_2F_4 addition to fluoroethene at 80° in a pressure reactor	All of the N_2F_4 was consumed. Product detonated during the removal from reactor.

be based on known chemical reactivity of this compound and on techniques that have been developed in working with perfluoroguanidine as reported by Esso Research and Engineering Co. (Ref 8), Rohm and Haas Co. (Ref 9) and Minnesota Mining and Manufacturing Co. (Ref 10). The types of structures to be investigated and the methods of preparation are briefly outlined below.

(a) Tris(difluoramino)methyl Ethers, Esters and Acids

The tris and hexakis(difluoramino)methyl ethers can be obtained from perfluoroguanidine via the reactions shown in equation 3

$$(F_2N)_2C{=}NF \xrightarrow[2.\ F_2]{1.\ ROH} (F_2N)_2COR \qquad (3)$$

where R = $-CH_3$, $-C_2H_5$, n-C_3H_7, iso-C_3H_7, n-C_4H_9, iso-C_4H_9, and t-C_4H_9.

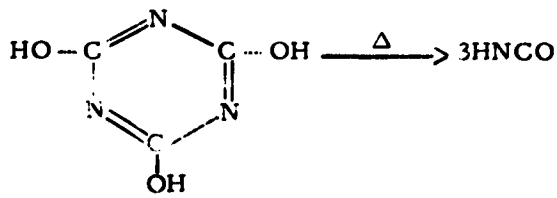
The series will also include cyclic alcohols. By employing glycols, diethers containing two tris(difluoramino) groups will be prepared:

$$(F_2N)_2C{=}NF \xrightarrow[2.\ F_2]{1.\ HOCH_2(CH_2)_nCH_2OH} (F_2N)_2COCH_2(CH_2)_nCH_2OC(NF_2)_3 \qquad (4)$$

where, n = 0-14.

(b) N-Tris(difluoramino)methyl Carbamate

Another interesting class of tris difluoramino compounds is available from tris(difluoramino)methylisocyanate, $(F_2N)_3CNCO$. If this compound is not available from other laboratories, it will be prepared by the known reaction of perfluoroguanidine with isocyanic acid, followed by mild fluorination. The isocyanic acid required in this work can be prepared by pyrolysis of cyanuric acid (Ref 11). The entire sequence of reactions can be written as follows:



$$\xrightarrow{\Delta} 3HNCO \qquad (5)$$

$$(F_2N)_2C{=}NF + HNCO \longrightarrow (F_2N)_2C(NFH)NCO \quad (6)$$

$$(F_2N)_2C(NFH)NCO + F_2 \longrightarrow (F_2N)_3CNCO \quad (7)$$

The tris(difluoramino)methyl isocyanate can then be utilized in the preparation of a series of carbamates and dicarbamates.

$$(F_2N)_3CNCO \xrightarrow[2.\ F_2]{1.\ ROH} ROCNHC(NF_2)_3 \quad (8)$$

Where, R = $-CH_3$, $-C_2H_5$, n-C_3H_7, iso-C_3H_7, n-C_4H_9, iso-C_4H_9.

$$(F_2N)_3CNCO \xrightarrow[2.\ F_2]{1.\ HOCH_2(CH_2)_nCH_2OH} (F_2N)_3CNHCOCH_2(CH_2)_nCH_2OCNHC(NF_2)_3 \quad (9)$$

where, n = 0-10.

(e) Facility for Synthesis of Tris(difluoramino) Compounds

Owing to the extreme shock sensitivity of perfluoroguanidine and many of its derivatives, it is necessary that all work with these materials be carried out behind the barricades provided with remote-control equipment. During the current report period, a considerable effort was devoted to the modification of an outside barricade for this work and to fabrication of a glass and metal vacuum system for conducting experiments with perfluoroguanidine.

The barricade unit (Figures 2 and 3) was constructed of plywood-covered half-inch steel (working area of 58 ft^2 and control room 65 ft^2). The roof of the building was made of a light material and only loosely attached to the walls to prevent pressure buildup in the event of an explosion. Manipulation of valves and stopcocks on the vacuum line and certain other necessary operations can be done by use of an Mini Manip arm.* A safety window made of 5/8-inch Butacite laminate permits observation of the operating area.

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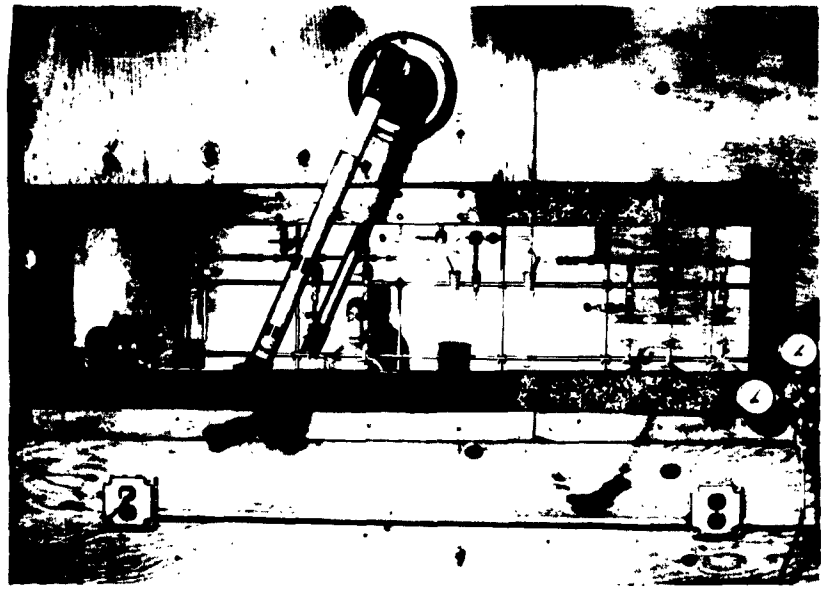
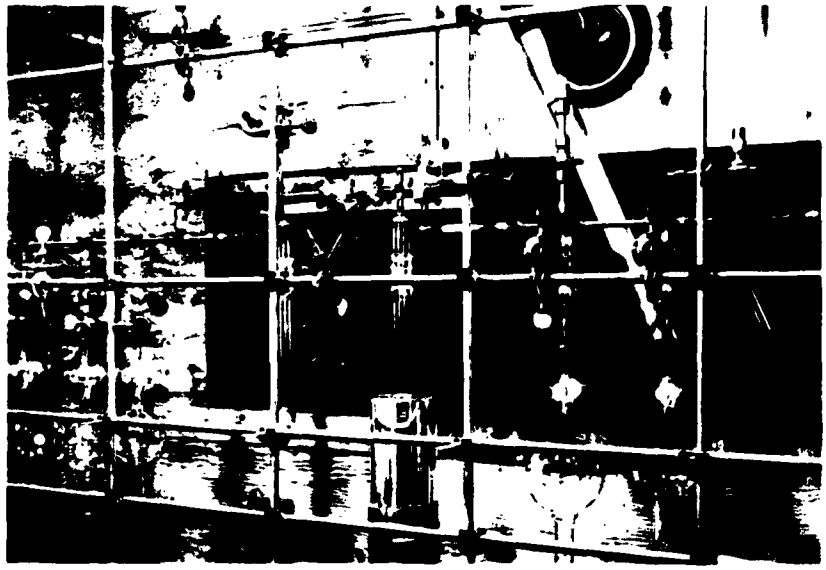
*Made by the AMF Atomics, Division of American Machine and Foundry Co., Greenwich, Conn.



(5007-1)

Figure 2. Control Area of Hazardous Laboratory



(5007-1)

Figure 3. Vacuum System in the Hazardous Laboratory

Crude perfluoroguanidine is stored in a tank outside the barricade in a specially constructed temperature controlled housing (Figure 4). From this tank measured amounts of crude perfluoroguanidine were condensed into the vacuum rack (Figure 5) and purified by trap-to trap distillation at -110°.

The mass spectral analysis of crude perfluoroguanidine received from Callery Chemical Co. showed it to be 16.6% pure, the rest being Compound R, SiF_4, NF_3, BF_3, N_2F_2, CO_2, O_2, and nitrogen oxides.

Work has been started on the evaluation of experimental conditions involved in perfluoroguanidine-alcohol reaction and subsequent fluorination of the fluoramino adduct.

During one purification run of perfluoroguanide, a violent explosion took place. Also, several detonations occurred in working with difluoramine and tetrafluorohydrazine. Due to proper safety procedures there were no personnel injuries and material losses were small.

B. REFERENCES

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3. M. J. Kamlet, A Correlation of Impact Sensitivities with Oxidant Balances, NAVORD Report (NOL) 6124, 26 September 1958.

4. J. M. Rosen, J. R. Holden, D J. Glover, The Thermal Sensitivity of NF Compounds, U.S Naval Ordnance Laboratory, NOLTR 63 178, 24 July 1963.

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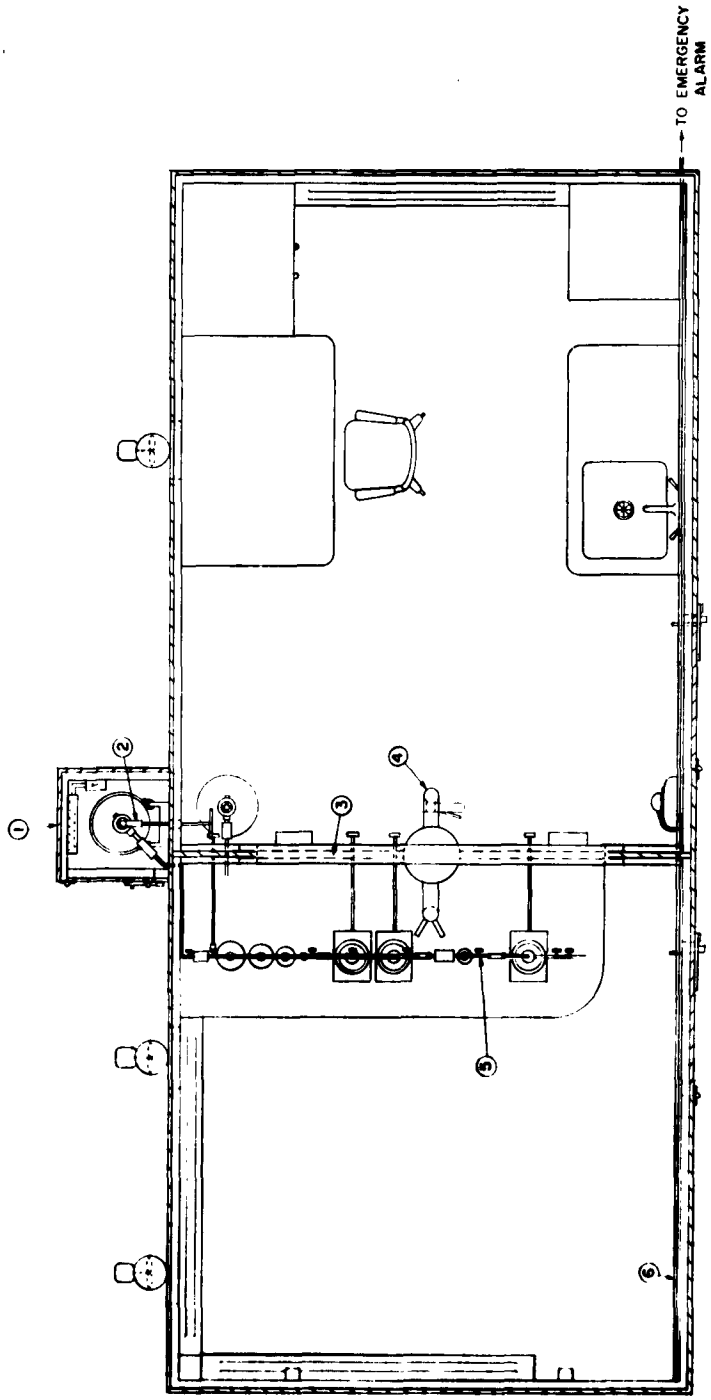
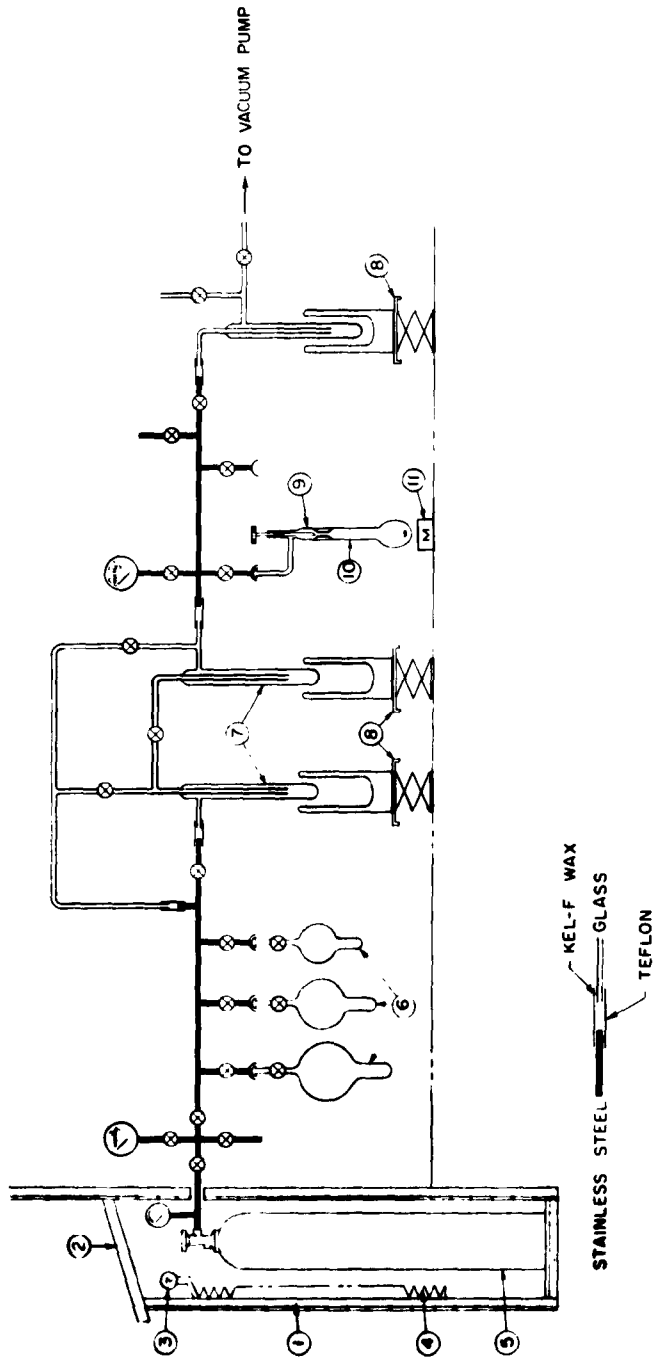
6. E. C. Horning (Editor), Organic Synthesis, Vol. III, John Wiley and Sons, Inc., New York, 1955, p 846



LEGEND

1. Outside barricade for storage of crude perfluoroguanidine at 15-25°.
2. Remote-control lever.
3. 5/8 inch Butacite laminate window.
4. Mini Manip remote-control arm.
5. Vacuum rack.
6. Emergency alarm.

Figure 4. Diagram of Hazardous Laboratory



LEGEND

1. Glass wool insulated steel barricade.
2. Blow out roof.
3. Thermostat.
4. 1600-watt electric heaters.
5. Perfluoroguanidine cylinder.
6. Storage flasks.
7. Traps for condensing perfluoroguanidine.
8. Remotely controlled Lab-Jacks.
9. Teflon Fisher-Porter valve.
10. Thick glass reactor (10 to 25 ml capacity).
11. Magnetic stirrer.

Figure 5. Schematic Diagram of Vacuum System for Perfluoroguanidine Studies

7. E. A. Lawton and J. R. Weber, J. Am. Chem. Soc . 81, 4755(1959).

8. Esso Research and Engineering Co , Quarterly Progress Report, No. 63-2, Research on Advanced Solid Propellants 10 June 1963.

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10. Minnesota Mining and Manufacturing Co. Chemical Research as Related to Advanced Solid Propellants Report No 17. 30 June 1963.

11. F. Zobrist, H. Schinz, Helv. Chim. Acta, 35 2380-88(1952).

Section III

RMD Project 5017

(U)
STABILIZATION OF HIGH ENERGY SOLID OXIDIZER

CONFIDENTIAL

Thiokol
REACTION MOTORS DIVISION

Section III

STABILIZATION OF HIGH ENERGY SOLID OXIDIZER

A. R. Young
J. J. Dvorak

Report RMD-AOR-ATS-63

RMD Project 5017
Report Period: 1 January 1963 to
31 December 1963

Contract No. NOnr 3913(00)
ARPA Order No. 354
Project Code 2910

CONFIDENTIAL

This report has been distributed in accordance with a combined LPIA-SPIA Distribution List in effect as of the publication date of this report.

FOREWORD

This section of the report summarizes the work carried out during the period from 1 January 1963 to 31 December 1963 on the chemical stabilization of nitronium perchlorate under Navy Contract NOnr 3913(00), ARPA Order No. 354.

Contributors to this study are A. R. Young, II (Project Supervisor), J. Dvorak (Principal Investigator), E. Egbert (X-ray Analysis), J. Creatura (Wet Chemical Analysis).

CONTENTS

ILLUSTRATIONS

TABLES

ABSTRACT

Reactions of nitronium perchlorate with potential coordinating ligands have been explored. The reagents investigated as coordinating ligands for the nitronium ion include: NO, $NOCl$, NOF, H_2O, Sulfolane, N_2F_4, cis-N_2F_2, and NF_3O. No evidence has been obtained for the existence of a stable nitronium perchlorate complex.

The reactions of NO, $NOCl$, and NOF with nitronium perchlorate yielded nitrosyl perchlorate. NO_2 was found to promote the autodecomposition of NO_2ClO_4 to $NOClO_4$ and O_2. No reactions were obtained with N_2F_2, N_2F_4 or NF_3O. Attempts to form a complex with $(CH_3)_3N$ and NO_2BF_4 resulted in a complex oxidation reduction reaction which produced NO, NO_2, N_2O, N_2, and $(CH_3)_3NBF_3$.

Preliminary studies of the possible existence of salts of the $NON_2H_5^{+2}$ or $NO_2N_2H_5^{+3}$ cations have not as yet given positive results.

I. INTRODUCTION

Reactions of nitronium perchlorate with potential coordinating ligands have been explored as a route to a more stable form of nitronium perchlorate. It was hoped that: (a) the existence of nitronium ion complexes $[NO_2(ligand)^+]$ in the solid state could be demonstrated, and (b) that the resultant complex nitronium ion perchlorates $[NO_2(ligand)^+ ClO_4^-]$ might show significantly reduced reactivity over that of NO_2ClO_4 to permit their use in solid propellant grains without prior physical coating.

Attempts to prepare such complex perchlorates by introducing NO, NOCl, or NOF as ligands to the nitronium ion in nitronium perchlorate, though unsuccessful, revealed some interesting aspects of the chemistry of nitronium perchlorate. The results of these experiments are written up at the beginning of the report in the form of a paper to be submitted for publication in Inorganic Chemistry.

Other approaches to the preparation of nitronium perchlorate complexes are described in the appendix. The work discussed in the appendix represents either incomplete studies or studies which are complete but which gave negative results and are not felt to be of sufficient interest to warrant publication.

II. MANUSCRIPT OF PAPER FOR PUBLICATION

The Reactions of Nitronium Perchlorate and Nitronium Fluoborate with Nitric Oxide, Nitrosyl Chloride and Nitrosyl Fluoride

[Prepared for Submission to Inorganic Chemistry]

Contribution from the Chemistry Department, Reaction Motors Division, Thiokol Chemical Corporation, Denville, N. J.

The Reactions of Nitronium Perchlorate and Nitronium Fluoborate with Nitric Oxide, Nitrosyl Chloride and Nitrosyl Fluoride

(Prepared for submission to Inorganic Chemistry)
by J. Dvorak and A. R. Young, II

NO_2ClO_4 and NO_2BF_4 react with NO, $NOCl$, and NOF in various solvent media and without a solvent to yield the corresponding nitrosonium salts. In the reactions with NO, one of the by-products, NO_2, catalyzes the auto-decomposition of nitronium salts to nitrosonium salts $NO_2ClO_4 \xrightarrow{NO_2} NOClO_4 + \frac{1}{2}O_2$).

INTRODUCTION

Solutions containing the nitrosonium cation absorb nitric oxide forming the complex cation $N_2O_2^+$[1,2,3], and salts of this cation are reported to exist in the solid state under high pressure and low temperature conditions.[4]

(1) W. Manchot, Z. Angew Chem., 25, 1655 (1912).

(2) F. Seel, et al., Z. Naturforsch. 8b, 607 (1953).

(3) F. See., Z. Angew Chem., 68, 272 (1956).

(4) F. Seel, "Recent Aspects of the Inorganic Chemistry of Nitrogen", Special Publication No. 10, The Chemical Society, London (1957).

Similarly, it is reported [5] that solutions of the nitronium cation absorb nitric

(5) J. Goulden, C. Ingold, and D. Miller, Nature, 165, 565 (1950).

oxide to yield the complex cation, $N_2O_3^+$.

We have attempted the preparation and isolation, in the solid state under ambient conditions, of salts of the cations, $N_2O_3^+$, $N_2O_3Cl^+$, and $N_2O_3F^+$, by reacting nitronium perchlorate and nitronium fluoborate with nitric oxide, nitrosyl chloride, and nitrosyl fluoride, respectively. In each instance the nitronium salt was converted to its corresponding nitrosonium salt. It was further determined that nitrogen dioxide catalyzes the autodecomposition of nitronium salts to nitrosonium salts and oxygen.

DISCUSSION

A. Reaction of NO_2ClO_4 with NO

The preparation of $N_2O_3ClO_4$ in the solid state was attempted initially by means of an equimolar gas-solid reaction. When NO was condensed onto NO_2ClO_4 at -196°C and then allowed to warm to room temperature, a brown color was observed in the gas phase. Upon recondensing the gas phase, the condensate showed the characteristic blue color of N_2O_3. Complete consumption of the initial NO was indicated when the blue color of N_2O_3 was absent at low temperatures. The brown gas which appeared on warming the system to room temperature was identified as NO_2 by mass spectroscopy and the solid

phase was shown to be $NOClO_4$ by x-ray (Figure 1) and wet chemical analysis. The reaction of NO with an equimolar amount of NO_2ClO_4 dissolved in acetonitrile gave identical results, with the $NOClO_4$ appearing as an insoluble product. Similar results were obtained in other reaction media as shown in Table I.

These results seemed to indicate the occurrence of the simple oxidation-reduction process shown in equation 1. However, observations made on the

$$NO + NO_2ClO_4 \longrightarrow NOClO_4 + NO_2 \qquad (1)$$

reaction of NO with two moles of NO_2ClO_4 in acetonitrile indicated that the process is more complex than shown in equation 1. Upon permanent discharge of the blue color of N_2O_3 (indicating complete consumption of NO), a small additional amount of NO was condensed into the reactor. The blue color of N_2O_3 reappeared and, surprisingly, it was not discharged by further reaction of NO with what had been thought to be an excess of NO_2ClO_4. The solid product obtained in this run was identified as pure $NOClO_4$ by x-ray analysis (Figure 1). Since the initial ratio of NO_2ClO_4 to NO was 2:1, it was apparent that some reaction other than that shown in equation 1 was responsible for the complete conversion of NO_2ClO_4 to $NOClO_4$.

A plausible explanation of this result is that NO_2 serves as a catalyst for the autodecomposition of NO_2ClO_4 (equation 2). The catalytic action might

$$NO_2 + NO_2ClO_4 \longrightarrow NOClO_4 + 1/2\ O_2 + NO_2 \qquad (2)$$

Table I

Reactions of Nitronium Salts with NO, NO_2, NOF and NOCl

Nitronium Salt Used	Gaseous Reagent	Mole Ratio of Reactants	Reaction Medium	Gaseous Products	Solid Products
NO_2ClO_4	NO	1:1	gas-solid	NO_2	$NOClO_4$
NO_2ClO_4	NO	2:1	gas-solid	NO_2, O_2	**
NO_2ClO_4	NO	2:1	CH_3CN solution	NO_2, N_2, trace O_2	$NOClO_4$
NO_2ClO_4	NO	2:1	CH_3NO_2 solution	N. D. *	$NOClO_4$
NO_2ClO_4	NO	2:1	SO_2 suspension	N. D. *	$NOClO_4$
NO_2ClO_4	NO_2	excess NO_2	liquid NO_2	N. D. *	$NOClO_4$
NO_2ClO_4	NOCl	1:1.5	liquid-solid	N. D. *	$NOClO_4$
NO_2ClO_4	NOCl	2:1	liquid-solid	NO_2Cl	***
NO_2ClO_4	NOF	1:1	gas-solid	N. D. *	$NOClO_4$
NO_2ClO_4	NOF	1:1	HF suspension	N. D. *	$NOClO_4$
NO_2BF_4	NO	1:1	gas-solid	NO_2	$NOBF_4$
NO_2BF_4	NO	2:1	CH_3CN solution	N. D. *	$NOBF_4$

* Not determined.

** X-ray powder pattern appears to be a mixture of NO_2ClO_4 and $NOClO_4$ presumably from inadequate mixing of reagents.

*** X-ray powder pattern appears to be a mixture of NO_2ClO_4 and $NOClO_4$.

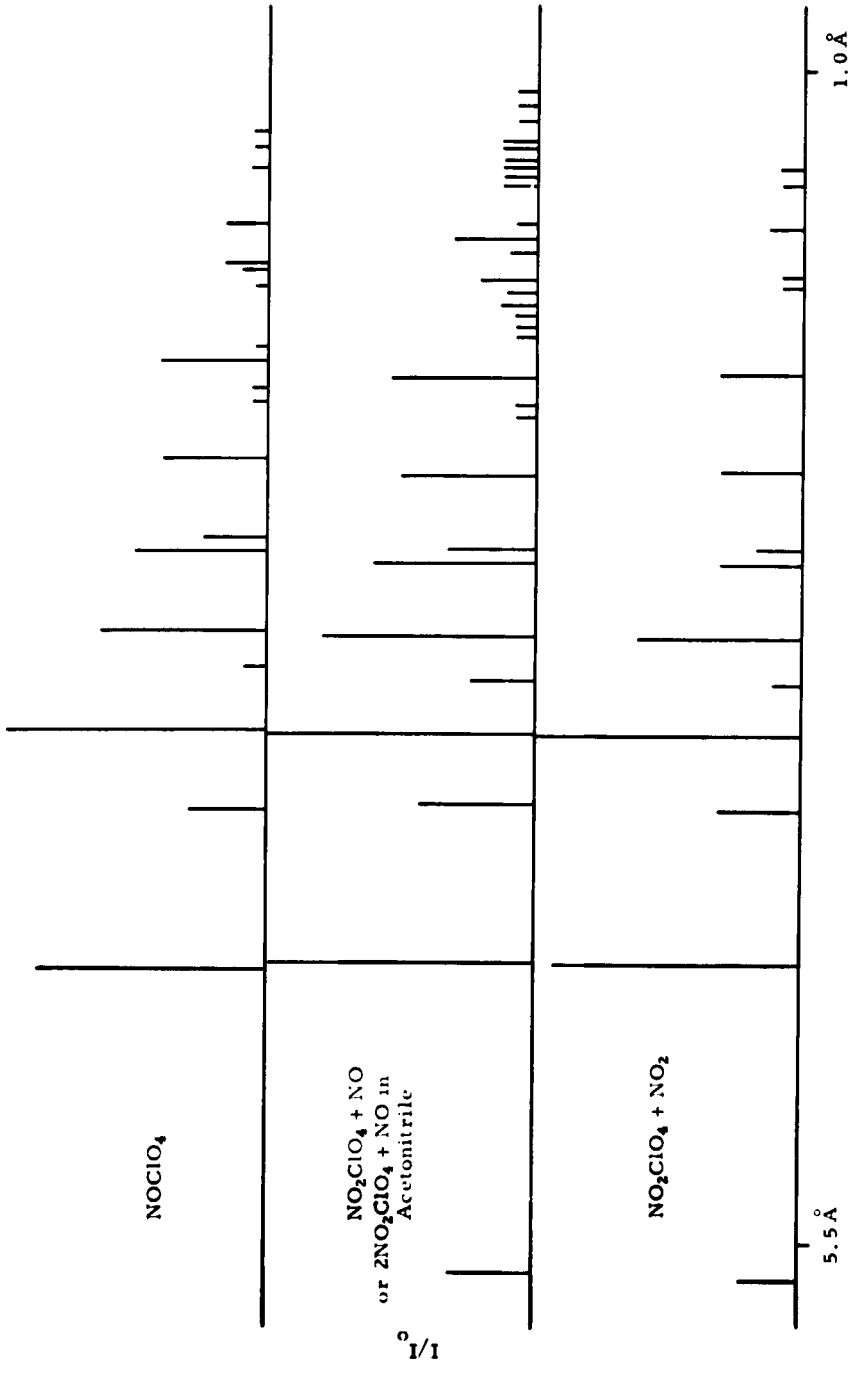

Figure 1. X-ray Diffraction Patterns. Products of $NO-NO_2ClO_4$ and $NO_2-NO_2ClO_4$ Reactions

proceed through the intermediate formation of N_2O_5 (equations 3, 4, 5). The

$$2NO_2 \underset{\longrightarrow}{\overset{\Delta}{\longleftarrow}} N_2O_4 \qquad (3)$$

$$N_2O_4 + NO_2ClO_4 \longrightarrow NOClO_4 + NO_2NO_3(N_2O_5) \qquad (4)$$

$$NO_2NO_3 \longrightarrow N_2O_4 + 1/2\ O_2 \qquad (5)$$

reaction of NO with NO_2ClO_4 was repeated in the absence of a solvent and the gaseous products were examined more carefully to determine whether a fraction not condensable at $196^{\circ}C$ was present. The presence of oxygen in addition to NO_2, as predicted by equation 2, was confirmed in this way. When the reaction was carried out in acetonitrile only a trace of oxygen was detected, but it is quite possible that the oxygen (or N_2O_5) was consumed by reaction with acetonitrile. Finally, NO_2ClO_4 was treated with NO_2 and was shown by x-ray analysis (Figure 1) to undergo conversion to $NOClO_4$. On the basis of these results a more complete overall representation of the reaction of NO with NO_2ClO_4 is given by equation 6

$$2NO_2ClO_4 + NO \longrightarrow 2NOClO_4 + NO_2 + 1/2\ O_2 \qquad (6)$$

B. Reactions of NO_2ClO_4 with NOCl and NOF

The reactions of NOCl and of NOF with NO_2ClO_4 were examined as possible routes to $N_2O_5Cl^+ClO_4^-$ and $N_2OF^+ClO_4^-$, respectively. In each case $NOClO_4$ was obtained as a product (see x-ray patterns, Figure 2), and the reactions proceeded as shown in equation 7.

$$NO_2ClO_4 + NOCl(NOF) \longrightarrow NOClO_4 + NO_2Cl(NO_2F) \qquad (7)$$

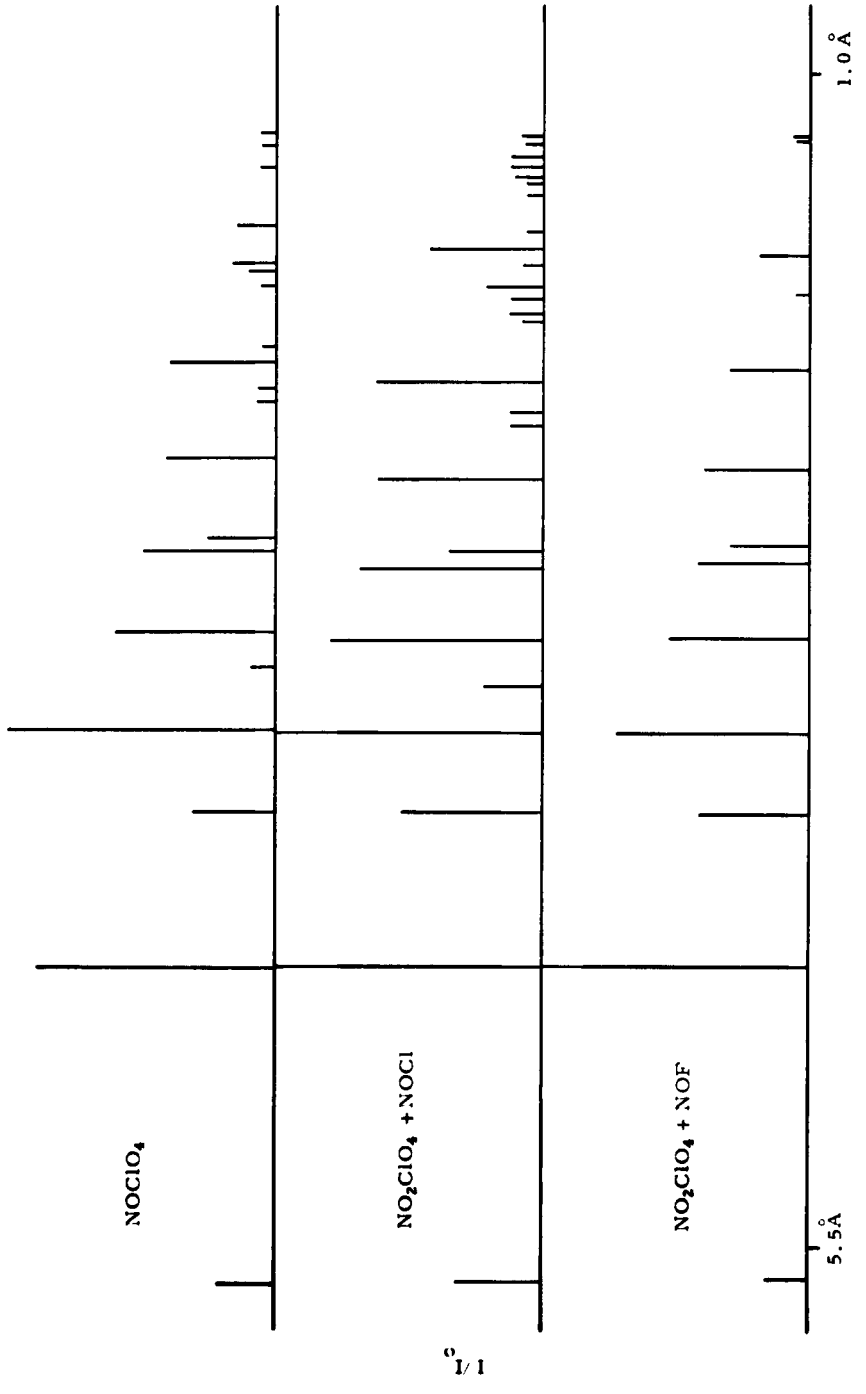

Figure 2. X-ray Diffraction Patterns. Products of $NOCl-NO_2ClO_4$ and $NOF-NO_2ClO_4$ Reactions

C. Reaction of NO_2BF_4 with NO

The reaction of NO_2BF_4 with NO is completely analogous to that of NO_2ClO_4 with NO and can be described adequately by the overall reaction shown in equation 8.

$$NO + 2NO_2BF_4 \longrightarrow 2NOBF_4 + 1/2\ O_2 + NO_2 \qquad (8)$$

EXPERIMENTAL

Analytical Techniques

Considerable reliance was placed on x-ray analysis of reaction products. The x-ray powder patterns of NO_2ClO_4, $NOClO_4$ and a 50% mixture of NO_2ClO_4/$NOClO_4$ were determined on our own instrument for comparison with the x-ray powder patterns of reaction products (Figures 1 and 2).

Since the x-ray powder patterns of $NOBF_4$ and NO_2BF_4 did not exhibit sufficiently significant differences, differential thermal analysis was utilized, in addition to wet analysis, for the characterization of NO_2BF_4-NO products (Figure 3).

The importance of a reliable functional group analysis in ascertaining the composition of "nitroxy" perchlorates by wet chemical methods is shown by comparing theoretical elemental and functional group compositions for $NOClO_4$, NO_2ClO_4 and a 50% mixture of NO_2ClO_4/$NOClO_4$ (Table II). Investigation of analytical methods for NO^+ and NO_2^+ resulted in the selection of NO^+ as the

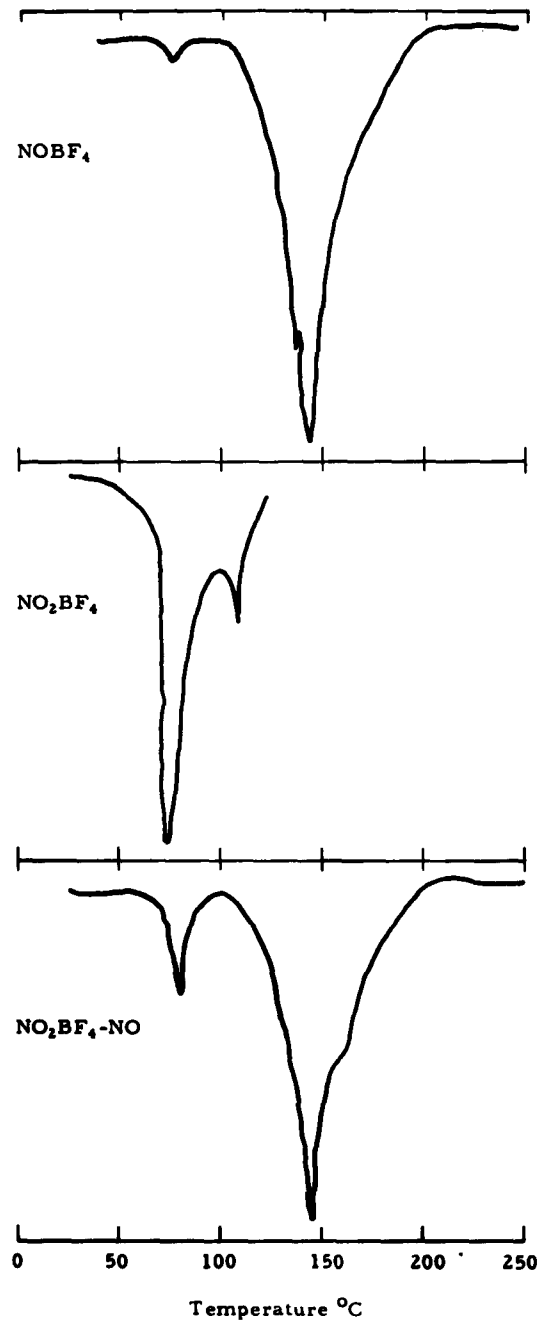

Figure 3. Differential Thermogram of NO-NO_2BF_4 Reaction Product

functional group which could be determined most reliably. Analysis for NO^+ was performed by hydrolytic conversion of this cation to NO_2^-, followed by titration with standard ceric sulfate. In this method, low results are obtained if the hydrolysis is not carried out at a sufficiently low temperature to prevent the reduction of NO^+ to NO. Before the cold solution is allowed to warm to room temperature, excess standard ceric sulfate is added. This is then back titrated with standard ferrous sulfate, the end-point being determined potentiometrically. This procedure was followed for samples of NO_2ClO_4, $NOClO_4$, the reaction products, and a prepared mixture of $NO_2ClO_4/NOClO_4$, containing 7.68% NO^+. The results are given in Table III.

Apparatus and Procedure

Most of the reactions described were conducted in Fischer and Porter Aerosol Compatibility Tubes fitted with a brass Bourdon tube pressure guage, a metal valve, and a ball joint for connection to the vacuum line. Those reactions in which a solvent was present were carried out in round bottom flasks fitted with a sintered glass disc, stopcock and ball joint. This assembly could be attached to the vacuum system and subsequently removed and inverted to filter the reaction mixture.

All sampling of solid reagents and preparation of solid products for analysis were carried out in a dry box.

Table II

Theoretical Compositions of Perchlorates

Atom or Group	Calcd for NO_2ClO_4 (%)	Calcd for $NOClO_4$ (%)	Calcd for 50% Mixture $NO_2ClO_4/NOClO_4$
N	9.62	10.85	10.18
Cl	24.39	26.94	25.81
NO^+	0.0	23.25	10.91
NO_2^+	31.61	0.0	16.72

Table III

Determination of NO^+ in Perchlorates and Fluoborates

Compound	NO^+ Found (%)	NO^+ Calcd (%)
$NOClO_4$*	22.6	23.25
NO_2ClO_4*	0.67	0.00
36 mole% $NOClO_4/NO_2ClO_4$	7.16	7.68
NO_2ClO_4 - NO Product	21.8	------
$2NO_2ClO_4$ - NO Product	22.6	------
50 mole % $NOClO_4/NO_2ClO_4$	----	10.91
$2NO_2ClO_4$ - NOCl Product	10.9	------
$NOBF_4$	----	25.68
$2NO_2BF_4$ - NO Product	24.2	------

* Obtained from Callery Chemical Company, Callery, Pennsylvania.

A. Reaction of NO_2ClO_4 with NO

1. Equimolar Reaction - To 0.5209 gm (3.57 mmoles) of NO_2ClO_4 at -196°C was added 3.6 mmoles of NO. The reaction mixture was allowed to warm slowly to room temperature with stirring. The gas was recondensed on the solid several times. The system was then evacuated and the white solid product was analyzed for the NO^+ group (Table III)

Anal. Calcd for NO^+: 23.3

Found: 21.8

2. Excess NO_2ClO_4 - To 1.183 gm (8.17 mmoles) of NO_2ClO_4 at -196°C was added 4.08 mmoles of NO. The reaction mixture was allowed to warm to room temperature slowly with stirring. After recondensing the gas on the NO_2ClO_4 several times the apparatus was then connected to the inlet system of the mass spectrometer and the gases, volatile at -196°C, -78°C and 25°C, were analyzed. Oxygen as well as NO_2 was found to be present. Apparently reaction was incomplete since x-ray analysis of the solid product appeared to be a mixture of $NOClO_4$ and NO_2ClO_4.

3. Excess NO_2ClO_4 in Liquid SO_2 - To a suspension of 0.340 gm (2.32 mmoles) of NO_2ClO_4 in 25 ml of SO_2 was added 1.16 mmoles of NO. The temperature of the reaction mixture was maintained at -10°C for several hours. The volatile materials were removed by vacuum distillation. The solid product was characterized as $NOClO_4$ by its x-ray powder pattern.

4. Excess NO_2ClO_4 in CH_3NO_2 - A solution of 0.490 gm (3.38 mmoles) of NO_2ClO_4 in 20 ml CH_3NO_2 was cooled to -196°C and 1.69 mmoles of NO was added. After warming to room temperature, the solution was stirred for several hours. The product was isolated by distillation of the solvent in vacuo and characterized as $NOClO_4$ by its x-ray pattern.

5. Excess NO_2ClO_4 in CH_3CN - To an acetonitrile solution of 0.7877 gm (4.72 mmoles) of NO_2ClO_4 at -196°C was added 2.36 mmoles of NO. After warming to room temperature a precipitate appeared. The reaction mixture was stirred for several hours. Then the noncondensable gases were transferred by means of a Toepler pump to a calibrated volume. The total noncondensable fraction evolved equaled 0.035 mmole. Mass spectroscopic analysis of these gases showed them to contain nitrogen and less than 10% O_2. The solid product was isolated by filtration and characterized as $NOClO_4$ by x-ray.

B. Reaction of NO_2ClO_4 with NOCl

These reactions were conducted in a manner similar to those described above for NO.

C. Reaction of NO_2ClO_4 with NOF

These reations were conducted in a Kel F reaction tube connected to a Monel vacuum system. The Kel F tube was charged with the NO_2ClO_4 followed by addition of anhydrous HF. Then a stoichiometric amount of NOCl was condensed on the reaction mixture with stirring. The HCl generated was

removed in vacuo. After stirring the reaction mixture several hours the product was isolated by removal of the volatile materials in vacuo. It was characterized as $NOClO_4$ by its x-ray diffraction pattern.

D. Reaction of NO_2BF_4 with NO

These reactions were conducted in a manner similar to those of NO_2ClO_4 with NO described in subsection A above.

Materials

$NOClO_4$ and NO_2ClO_4 were obtained from the Callery Chemical Company.

$NOBF_4$ and NO_2BF_4 were obtained from Ozark-Mahoning Company, Tulsa, Oklahoma.

III. APPENDIX - STABILIZATION OF NITRONIUM PERCHLORATE

A. INTRODUCTION

The reactions of nitronium perchlorate with potential coordinating ligands are being explored in an attempt to reduce the reactivity of nitronium perchlorate so that it can be used in solid propellant compositions without prior physical coating.

The results of unsuccessful attempts to utilize NO, NOCl, and NOF as nitronium ion ligands were presented in Section II. Other attempts to prepare nitronium perchlorate complexes have been pursued, such as the direct interaction of nitronium perchlorate with potential ligands—NF_3O, cis-N_2F_2 and N_2F_4. The preparation of a monohydrate of nitronium perchlorate was explored with the idea of obtaining a complex perchlorate capable of undergoing ligand exchange reactions to yield stable energetic nitronium ion complexes. More recent efforts have been directed toward the preparation of the nitrylhydrazinium ($NO_2N_2H_5^{+2}$) cation.

B. DISCUSSION

Two principal approaches have been pursued in an attempt to synthesize stable nitronium perchlorate complexes. The direct interaction of nitronium perchlorate with potential energetic ligands, such as NF_3O and N_2F_4, is illustrative of one approach. A second approach involved attempts to prepare nitronium ion complexes associated with anions other than perchlorate, which could subsequently be converted to perchlorates. The investigation of the reaction of $(CH_3)_3N$ with NO_2BF_4 serves as an example of this method.

1. Reaction of NO_2ClO_4 with cis-N_2F_2

An attempt was made to prepare a complex perchlorate by the direct interaction of cis-N_2F_2 with NO_2ClO_4 (equation 1). However, no reaction occurred

$$NO_2ClO_4 + N_2F_2 \not\longrightarrow NO_2\left[N_2F_2\right]ClO_4 \qquad (1)$$

between NO_2ClO_4 and gaseous or liquid cis-N_2F_2; both reagents were recovered.

2. Reaction of NO_2ClO_4 with NF_3O

An investigation of the preparation of a complex nitronium perchlorate by reaction with NF_3O was pursued (equation 2). A mixture of NF_3O and NO_2ClO_4

$$NO_2ClO_4 + NF_3O \not\longrightarrow NO_2\,[NF_3O]\,ClO_4 \qquad (2)$$

was allowed to react for several hours at temperatures from -196°C to 25°C. The gas phase contained principally NF_3O, with smaller amounts of SiF_4, NO_2 and ClO_3F. The solid phase gave an x-ray powder pattern consistent with that of NO_2ClO_4. Chemical analysis also indicated that NO_2ClO_4 was recovered unreacted.

A similar reaction was conducted with $NOClO_4$ and NF_3O (equation 3). The

$$NOClO_4 + NF_3O \not\longrightarrow NO\,[NF_3O]\,ClO_4 \qquad (3)$$

infrared spectrum of the gaseous phase was that of NF_3O and the x-ray pattern of the solid phase was that of $NOClO_4$. Analysis of the solid for NO^+ was close to the theoretical values for $NOClO_4$.

Since no reaction was found to occur between NF_3O and CH_3NO_2 or CH_3CN, attempts were made to carry out the addition of NF_3O to NO_2ClO_4 in these solvents. A CH_3CN solution of NO_2ClO_4 was cooled to -196°C and NF_3O was added. The reaction mixture was then allowed to warm slowly. At approximately -40°C, the reaction mixture detonated violently.

A similar run was conducted with CH_3NO_2 as a solvent and there was no indication of an exotherm. After the reaction mixture had been stirred for several hours at room temperature the gaseous fraction was isolated and found to contain principally SiF_4 with smaller amounts of ClO_3F, NF_3O, O_2 and NO_2. The CH_3NO_2 was removed in vacuo leaving a residual white solid. The x-ray powder pattern of the white solid shows the major diffraction lines of NO_2ClO_4, although there are some lines of moderate intensity not observed in the NO_2ClO_4 powder patterns. It is suggested that these slight discrepancies are due to trace impurities of $NOClO_4$ and CH_3NO_2.

3. Reaction of NO_2ClO_4 with N_2F_4

A single experiment was conducted in an attempt to add N_2F_4 to NO_2ClO_4 (equation 4). The N_2F_4 was condensed on NO_2ClO_4 at -196°C and allowed to

$$NO_2ClO_4 + N_2F_4 \not\longrightarrow NO_2\,[N_2F_4]\,ClO_4 \qquad 4)$$

warm slowly to room temperature. The evolved gases were recondensed on the solid phase several times. The gas phase was found to contain predominantly SiF_4 with lesser amounts of N_2F_4, SF_6, NO and NO_2. The solid product had an x-ray powder pattern consistent with that of $NOClO_4$. These results can be explained on the basis of the reaction of NO_2 with NO_2ClO_4 to yield $NOClO_4$. However, it is not known whether the NO_2 present came from an interaction of N_2F_4 with the glass vessel or from an interaction with NO_2ClO_4.

4. Reaction of NO_2ClO_4 with H_2O

Workers at Esso Research (Ref 1) have on handling NO_2ClO_4 occasionally noted changes in the x-ray powder diffraction patterns. These changes were attributed to the formation of a monohydrate of nitronium perchlorate, $NO_2ClO_4 \cdot H_2O$. Assuming that the water in the monohydrate is associated with NO_2^+, this is the only reported example of a nitronium ion complex existing in the solid state. Such a complex might be a useful reagent for the preparation of other, more energetic, complexes of nitronium perchlorate.

In a preliminary experiment, a quantity of concentrated nitric acid calculated to yield a monohydrate by reaction with NO_2ClO_4 was distilled onto the solid at -196°C and allowed to warm to room temperature. A pasty solid residue was formed which fumed considerably when handled in the dry box. The x-ray diffraction lines of this product (Ref 2) show no similarity to those of NO_2ClO_4, $NOClO_4$ or the proposed monohydrate of NO_2ClO_4.

In a second reaction, an equimolar amount of water was added to a nitromethane solution of NO_2ClO_4. Upon removal of the solvent in vacuo, only a trace of solid remained which was identified by its x-ray powder pattern as $NOClO_4$.

When an equimolar amount of water vapor was allowed in contact with a nitromethane solution of NO_2ClO_4 and the solvent later removed in vacuo, a pasty material was obtained which gave a negative qualitative test for NO^+ and NO_2^+ but a positive test for ClO_4^-. Presumably, the pasty mass is merely a perchloric acid hydrate.

5. Reaction of H_3OClO_4 with NOCl

An alternate route to the monohydrate of NO_2ClO_4 is illustrated by equation 5.

$$H_3OClO_4 + NO_2Cl \xrightarrow{?} NO_2ClO_4 \cdot H_2O + HCl \qquad (5)$$

The reaction of H_3OClO_4 with NOCl (equation 6) was initiated as a prototype

$$H_3OClO_4 + NOCl \xrightarrow{?} NOClO_4 \cdot H_2O + HCl \uparrow \quad (6)$$

reaction for the preparation of $NO_2ClO_4 \cdot H_2O$.

When NOCl was allowed to react with H_3OClO_4, a gas was evolved which was deep purple in color at -196°C. Mass spectroscopic analysis indicated the gas contained NO, NO_2, NOCl, Cl_2, and a material having a mass peak of 130. No HCl was detected. The reaction mixture contained a white solid and what appeared to be a colorless liquid. After drying the solid in a vacuum desiccator over P_2O_5, a material which had an x-ray powder pattern consistent with that of $NOClO_4$ (Ref 3) was obtained.

6. Reaction of NO_2ClO_4 with N_2H_5F

An attempt was made to prepare $NO_2N_2H_5(ClO_4)_2$ by the reaction of NO_2ClO_4 with N_2H_5Cl in liquid HF (equations 7, 8). A mixture of N_2H_5Cl and liquid HF

$$N_2H_5Cl + HF \longrightarrow N_2H_5F + HCl \quad (7)$$

$$NO_2ClO_4 + N_2H_5F \longrightarrow NO_2N_2H_5(ClO_4)_2 + NO_2F \quad (8)$$

was pumped at -78°C to remove the HCl generated. This mixture was then added to NO_2ClO_4 at -196°C and allowed to warm to room temperature. The mixture underwent a variety of color changes on warming to room temperature. Removal of the HF in vacuo yielded a yellow pasty mass which dried to a white solid after it was pumped for several hours. The x-ray powder pattern appears to be that of $NOClO_4$. Basic hydrolysis of the solid product resulted in the liberation of some NO, but neither N_2H_4 nor NH_3 was detected in the head vapors. Chemical analysis (Ref 4) also tends to confirm the conclusion that the desired product was not obtained.

7. Reaction of NO_2ClO_4 with N_2H_5Cl

Several reactions were conducted with the ultimate objective of preparing a double hydrazinium salt with NO_2ClO_4 (equation 9). The reactions of N_2H_5Cl

$$2NO_2ClO_4 + N_2H_5Cl \longrightarrow NO_2N_2H_5(ClO_4)_2 + NO_2Cl \quad (9)$$

with NOCl and with $NOClO_4$ were explored as prototype reactions (equations 10 and 11). No visible reaction occurred between H_2H_5Cl and NOCl below

$$N_2H_5Cl + NOCl \longrightarrow NON_2H_5Cl_2 \quad (10)$$

$$N_2H_5Cl + 2NOClO_4 \longrightarrow NON_2H_5(ClO_4)_2 + NOCl \quad (11)$$

$-5^{\circ}C$, but a vigorous reaction occurred above $-5^{\circ}C$. The gas phase consisted of N_2, N_2O, and HCl. The solid product, $N_2H_6Cl_2$, was identified by x-ray (Figure 4) and chemical (Table IV) analyses.

TABLE IV

ANALYSIS OF N_2H_5Cl-NOCl REACTION PRODUCT

Group	Found (%)	Calcd for $N_2H_6Cl_2$ (%)	Calcd for N_2H_5Cl (%)
N_2H_4	28.79	30.47	46.71

The N_2H_5Cl-NOCl reaction was repeated using a large excess of NOCl and maintaining the reaction temperature between $-64^{\circ}C$ and $-10^{\circ}C$ in the hope that the desired addition product could be obtained under these milder conditions. After complete removal of the excess NOCl at reduced temperatures, the solid was allowed to warm slowly to room temperature. No decomposition was observed. The x-ray powder pattern (Figure 4) is indicative of a mixture containing predominantly N_2H_5Cl and some $N_2H_6Cl_2$. Chemical analysis (Table V) confirms this conclusion.

TABLE V

ANALYSIS OF N_2H_5Cl-NOCl LOW TEMPERATURE PRODUCT

Group	Found (%)	Calcd for N_2H_5Cl (%)	Calcd for $N_2H_6Cl_2$ (%)
N_2H_4	38.66	46.71	30.47

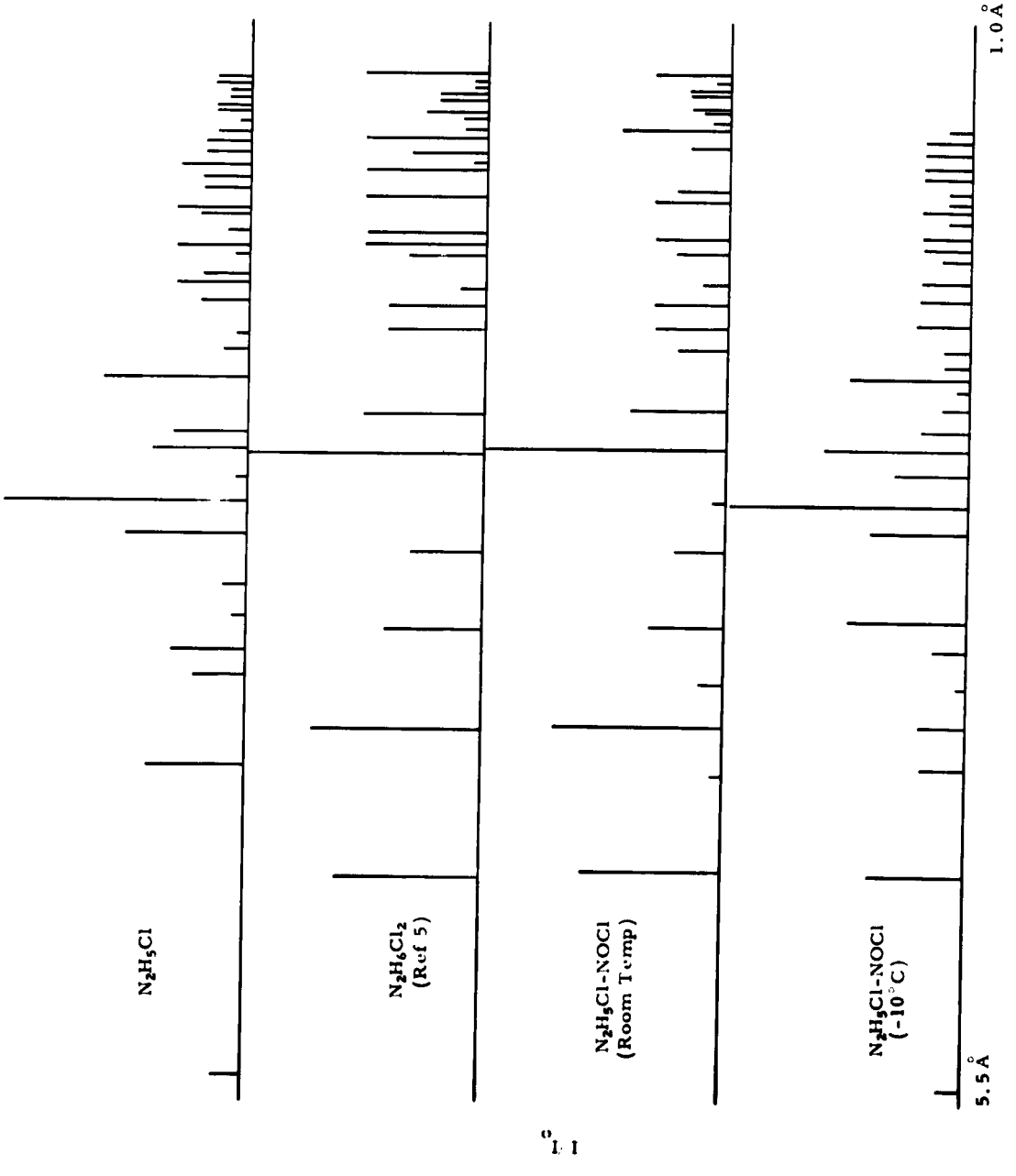

Figure 4. X-ray Diffraction Patterns. Products of N_2H_5Cl-NOCl Reactions

An attempt was made to prepare a 1:1 addition compound of $NOClO_4$ and N_2H_5Cl in liquid NOCl. The temperature of the system was maintained below -20°C to minimize the reaction between N_2H_5Cl and the solvent. The NOCl was removed in vacuo at -20°C and the solid residue was treated with acetonitrile. The acetonitrile insoluble fraction was predominantly $N_2H_6Cl_2$, the presence of which is attributed to the reaction of N_2H_5Cl with NOCl. The soluble fraction gave positive qualitative tests for $N_2H_5^+$ and ClO_4^- and negative tests for NO^+ and Cl^-. Its hydrazine content was 22.3%, which compares favorably with the value of 24.2% calculated for $N_2H_5ClO_4$. When this reaction was repeated, the acetonitrile soluble fraction again gave positive qualitative tests for $N_2H_5^+$ and ClO_4^- and negative tests for NO^+ and Cl^-. However, its hydrazine content was 10.13%, which compares more favorably with the value of 13.73% calculated for $N_2H_6(ClO_4)_2$. These results could be attributed to the interaction of $NOClO_4$ with N_2H_5Cl and $N_2H_6Cl_2$ (equations 12 and 13) accompanied by the liberation of NOCl. The presence of $N_2H_6Cl_2$ is accounted for by

$$NOClO_4 + N_2H_5Cl \longrightarrow N_2H_5ClO_4 + NOCl \qquad (12)$$

$$2NOClO_4 + N_2H_6Cl_2 \longrightarrow N_2H_6(ClO_4)_2 + 2NOCl \qquad (13)$$

the reaction of the solvent with N_2H_5Cl (equation 14).

$$N_2H_5Cl + NOCl \longrightarrow N_2H_6Cl_2 + \text{decomposition gases} \qquad (14)$$

Since an excess of one reagent might favor the formation of a uniform product, the reaction of $NOClO_4$ with N_2H_5Cl in a 2:1 mole ratio was carried out in NOCl at low temperatures. The solid product contained NO^+ by qualitative analysis. When the solid was treated with acetonitrile to effect a separation of the perchlorates from the chlorides, a vigorous reaction ensued and the solid decomposed. It was determined that decomposition of the 2:1 $NOClO_4$-N_2H_5Cl product in acetonitrile occurs at -40°C, as well as at room temperature. The decomposition gases consisted of N_2, N_2O and NO. Prior to treatment of the solid product with acetonitrile the ratio of NO^+ to N_2H_4 was determined on a small sample to be 6.6:1.0. Since a 2:1 ratio of $NOClO_4$ to N_2H_5Cl was used, the significant decomposition in hydrazine of N_2H_5Cl must have occurred in the NOCl medium.

It was thought that the $NOClO_4$-N_2H_5Cl reaction could be used as a method of preparation of $N_2H_5ClO_4$ in a solvent with which N_2H_5Cl does not react. $N_2H_5ClO_4$ is desired in order to attempt the preparation of $N_2H_5NO_2(ClO_4)_2$

as shown in equation 15. It was decided to attempt the preparation of $N_2H_5ClO_4$ in acetonitrile.

$$N_2H_5ClO_4 + NO_2ClO_4 \longrightarrow NO_2N_2H(ClO_4)_2 \qquad (15)$$

As in previous reactions, the solid reagents, N_2H_5Cl and $NOClO_4$, were mixed in the reaction vessel in the dry box. However, in this instance shortly after mixing the solids, a violent reaction ensued accompanied by deflagration. This may be due to an NO_2ClO_4 impurity in the $NOClO_4$. It had been determined that NO_2ClO_4 reacts violently with N_2H_5Cl in the solid state.

8. Reaction of NO_2ClO_4 with Sulfolane

Nitronium perchlorate was found to dissolve readily in Sulfolane (tetramethylene sulfone). Addition of chloroform, essentially a nonsolvent, did not result in precipitation of NO_2ClO_4. The solution, after hydrolysis, gave a positive test for ClO_4^- and a negative test for NO_3^-. Consequently, the reaction was repeated by adding an equimolar amount of Sulfolane to a suspension of NO_2ClO_4 in $CHCl_3$. A trace of NO_2ClO_4 (by x-ray analysis) remained undissolved and was separated by filtration. The filtrate again gave a positive test for ClO_4^- and a negative test for NO_3^- after hydrolysis.

When an equimolar amount of Sulfolane was added to NO_2ClO_4 suspended in Freon-113, a viscous oil was obtained. The Freon was separated and evaporated. No solids were present. The oil was triturated in CCl_4 to give a pasty solid. The infrared spectrum of the solid lacked definition and the solid decomposed before chemical analysis could be obtained.

9. Reaction of NO_2BF_4 with $(CH_3)_3N$

An attempt was made to prepare a complex nitronium ion by reaction of NO_2BF_4 with $N(CH_3)_3$ (equation 16)

$$NO_2BF_4 + N(CH_3)_3 \longrightarrow NO_2\left[N(CH_3)_3\right]BF_4 \qquad (16)$$

When $N(CH_3)_3$ was added to a solution of NO_2BF_4 in acetonitrile, a vigorous reaction ensued and N_2, N_2O, NO and NO_2 were evolved. The solid product obtained after removal of the acetonitrile gave a negative test for nitrate and nitrite ions. Trimethylamine is evolved upon basic hydrolysis. Chemical analysis (Ref 6) suggests the product is $(CH_3)_3N{:}BF_3$.

C. EXPERIMENTAL

Only the experimental work not included in previous reports (Ref 2 and 3) is described in this section.

The reactions were conducted in Fischer and Porter Aerosol compatibility tubes fitted with a pressure gauge, a metal valve and a ball joint for connection to the vacuum line.

All sampling of solid reagents was carried out in a dry box.

1. Reaction of NO_2ClO_4 with NF_3O

a. Gas-Solid Reaction

To 0.64339 gm (4.43 mmoles) of NO_2ClO_4 at -196°C was added 4.43 mmoles of NF_3O. The reaction mixture was allowed to warm to room temperature with stirring. The gases were recondensed on the solid several times. Analysis of the gaseous fraction showed that it contained predominantly NF_3O with SiF_4 and ClO_3F. X-ray analysis of the solid product showed it to be NO_2ClO_4.

Anal. Calcd for NO_2ClO_4: 9.62% N; 0.00% NO

Found 8.28% N; 0.02% NO

The reaction of $NOClO_4$ with NF_3O was conducted similarly. Both reactants were recovered.

Anal. Calcd for $NOClO_4$: 23.25% NO

Found 22.71% NO

b. Reaction in CH_3CN

To 0.6210 gm (4.28 mmoles) of NO_2ClO_4 at -196°C was first added approximately 20 ml of CH_3CN. Then 4.28 mmoles of NF_3O was condensed on the solid mixture. The reaction mixture was allowed to warm slowly. At approximately -40°C the reaction mixture detonated violently.

c. Reaction in CH_3NO_2

To 0.4290 gm (2.95 mmoles) of NO_2ClO_4 and approximately 20 ml of CH_3NO_2 was added at -196°C 2.95 mmoles of NF_3O. After warming to room temperature

the reaction mixture was stirred several hours. The gas phase consisted of NF_3O, ClO_3F, O_2 and NO_2. Removal of the solvent in vacuo resulted in recovery of NO_2ClO_4 determined by x-ray.

2. Reaction of NO_2ClO_4 with N_2F_4

To 0.43679 gm (3.00 mmoles) of NO_2ClO_4 at -196°C was added 3.00 mmoles of N_2F_4. After warming to room temperature the gases were recondensed several times. The gas phase was found to contain SiF_4, N_2F_4, NO and NO_2. The solid phase had an x-ray powder pattern consistent with that of $NOClO_4$.

3. Reactions Involving N_2H_5Cl

a. Room Temperature N_2H_5Cl - NOCl Reaction

To 0.815 gm (11.9 mmoles) of N_2H_5Cl at -196°C was added 12.0 mmoles of NOCl. The reaction mixture was allowed to warm slowly to room temperature. Above -5°C considerable fuming was observed and N_2, N_2O and HCl were evolved. The solid product $N_2H_5Cl_3$ was identified by x-ray and chemical analysis.

Anal. Calcd for $N_2H_5Cl_3$: 30.47% N_2H_4

Found 28.79% N_2H_4

b. Low Temperature N_2H_5Cl - NOCl Reaction

To 0.2521 gm (3.68 mmoles) of N_2H_5Cl at -196°C was added a large excess of NOCl. The reaction mixture temperature was then maintained between -50°C and -10°C for several hours with stirring. After removal of the NOCl at -10°C in vacuo a white solid was obtained which had an x-ray powder pattern indicative of a mixture containing predominantly N_2H_5Cl with some $N_2H_5Cl_3$.

Anal. Calcd for N_2H_5Cl: 46.7% N_2H_4

Found 38.66% N_2H_4

c. Reaction of $NOClO_4$ with N_2H_5Cl

To a mixture of 0.2146 gm (1.63 mmoles) of $NOClO_4$ and 0.1116 gm (1.63 mmoles) of N_2H_5Cl at -196°C was added a large excess of NOCl. The

reaction mixture temperature was then maintained between -50° and -20°C for several hours. After removal of the solvent in vacuo the residual solid was treated with acetonitrile to yield an insoluble fraction ($N_2H_6Cl_2$ by x-ray) and a soluble fraction. The acetonitrile was removed in vacuo to yield a solid which gave a positive test for N_2H_4 and ClO_4^- and a negative test for NO^+.

Anal. Calcd for $N_2H_5ClO_4$: 22.3% N_2H_4

Found: 24.2% N_2H_4

In a second run the acetonitrile soluble solid was found to have a hydrazine content which compares more favorably with $N_2H_6(ClO_4)_2$.

Anal. Calcd for $N_2H_6(ClO_4)_2$: 13.73% N_2H_4

Found 10.13% N_2H_4

The reaction of excess $NOClO_4$ with N_2H_5Cl described in the discussion was conducted in a manner similar to the stoichiometric reaction illustrated above.

CAUTION: In one instance mixing solid $NOClO_4$ and N_2H_5Cl resulted in an extremely violent reaction.

d. Reaction of NO_2ClO_4 with N_2H_5Cl

Shortly after mixing NO_2ClO_4 and N_2H_5Cl in the Fischer and Porter reactor, the pressure rose suddenly to 50 psi and most of the gases were released. A sample of the gases was obtained for analysis and found to contain N_2, Cl_2, NO_2, and H_2O. No significant amount of solid remained.

D. REFERENCES

1 Esso Research Corporation Quarterly Report No 61-2, DA-30-069-ORD 2487, March to June 1961.

2 Report RMD 5017-Q1, Stabilization of High Energy Solid Oxidizer, Thiokol Chemical Corporation, Reaction Motors Division, 30 November 1962, p. 9 (Contract NOrr 39(3)-00).

3. RMD Project 5017, RMD AOR Q3-63, Advanced Oxidizer Research, 31 October 1963, p. 9 (Contract NOrr 39(3)-00).

4. Ibid, p. 10

5 Chemical Service Department, United Kingdom Atomic Energy Authority, Windscale, England.

6. RMD Project 5017 RMD AOR Q2-63 Advanced Oxidizer Research, 30 April 1963, p. 6 (Contract NOrr 39(3)-00).

Section IV

RMD Project 5009

INORGANIC CHEMISTRY OF THE OXYGEN SUBFLUORIDES

Thiokol
REACTION MOTORS DIVISION

Section IV

INORGANIC CHEMISTRY OF THE OXYGEN SUBFLUORIDES

A. R. Young
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Report RMD AOR-ATS-63

RMD Project 5009
Report Period. 16 January 1963 to
31 December 1963

Contract No. NOnr 3824(00)
ARPA Order No. 314
Project Code 9100

This report has been distrubited in accordance with a combined LPIA-SPIA Distribution List in effect as of the publication date of this report.

FOREWORD

This report summarizes the results of studies of the chemistry of dioxygen difluoride during the period from 16 January 1963 to 31 December 1963 under Navy Contract NOnr 3824(00), ARPA Order No. 314.

Personnel directly involved in these studies were: A. R. Young, II (Project Supervisor), T. Hirata, S. Morrow, and K. Tiger. Analytical support was contributed by R. Storey, D. Yee, A. Fremmer, and E. Egbert.

CONTENTS

ILLUSTRATIONS

ABSTRACT

The preparation and properties of dioxygenyl salts of the hexafluorophosphate, hexafluoroarsenate, and hexafluoroantimonate anions were investigated and the results are presented in a reprint from the Journal of the American Chemical Society. Reactions of O_2AsF_6 with a large number of inorganic agents were investigated. No satisfactory solvent has been found for O_2AsF_6 at room temperature but solutions in HF appeared to be stable between -80 and -50°C. O_2AsF_6 solutions in HF are violet and transient violet solutions were also observed when O_2AsF_6 was mixed with SbF_5 and SO_2Cl_2 at room temperature.

Reactions of O_2F_2 with Xe, $SnCl_4$, NF_3O, and POF_3 failed to produce stable dioxygenyl salts.

Low temperature infrared studies of O_2F_2 and its reaction products were initiated. Spectra are presented of O_2F_2, the O_2F_2-Cl_2 reaction product, the O_2F_2-HCl reaction product, and the O_2F_2-AsF_5 reaction product.

I. INTRODUCTION

This research program is an investigation of the chemical properties of the subfluorides of oxygen, O_2F_2, O_3F_2, and O_4F_2. It is hoped that information obtained from a study such as this will suggest methods of synthesizing new inorganic oxidizers having O-F bonds.

During the period from January 15, 1963 to December 31, 1963, we confined our study to the chemistry of dioxygen difluoride (O_2F_2). Most of our effort was utilized in the characterization of reaction products of O_2F_2 with Group V pentafluorides. These products were shown to be salts of the dioxygenyl cation (O_2^+) having the general composition, O_2MF_6. The preparation and characterization of dioxygenyl salts of the pentafluorides of phosphorous, arsenic, and antimony represent a completed phase of our study and have been published in the January 1964 issue of the Journal of American Chemical Society under the title, "The Preparation of Dioxygenyl Salts from Dioxygen Difluoride." A reprint of the paper comprises Section II of this report.

The remaining studies undertaken, but not completed, during this report period are discussed in the Appendix (Section III). These include:

a. Reactions of O_2F_2 with various inorganic reagents

b. Preliminary studies of the chemistry of dioxygenyl salts

c. A study of the chemistry of O_2F_2 by means of low temperature infrared spectroscopy.

II. MANUSCRIPT OF PAPER FOR PUBLICATION

The Preparation of Dioxygenyl Salts from Dioxygen Difluoride

[Reprinted from J. Am. Chem. Soc. 86, 20 (1964)]

[Contribution from the Chemistry Department, Reaction Motors Division, Thiokol Chemical Corporation, Denville, N.J.]

The Preparation of Dioxygenyl Salts from Dioxygen Difluoride

A. R. Young, II, T. Hirata and S. I. Morrow

Dioxygen difluoride reacts at temperatures near its melting point (-163.5°C) with the pentafluorides of phosphorus, arsenic and antimony to give solid products which behave as strong oxidizers. Chemical evidence as well as infrared and X-ray diffraction data support a characterization of these solids as dioxygenyl salts, O_2MF_6 (M=P, As, or Sb). O_2PF_6 is unstable at room temperature, but O_2AsF_6 and O_2SbF_6 are stable to above 100°C in an inert atmosphere.

INTRODUCTION

The synthesis of the thermally unstable compound, dioxygen difluoride, was first reported by Ruff and Menzel[1] in 1933. Nothing was published about its chemical properties until the recent appearance of reports of its reactions with tetrafluoroethylene,[2] with chlorine monofluoride,[3] and with a variety of inorganic reagents.[4] During the course of a continuing investigation of its chemical

(1) O. Ruff and W. Menzel, Z. Anorg. Chem., 211, 204 (1933).

(2) R. T. Holzmann and M. S. Cohen, Inorg. Chem., 1, 972 (1962).

(3) A. G. Streng and A. V. Grosse, A. C. S. Advances in Chemistry Series, No. 36, pages 159-165 (1962).

(4) A. G. Streng, J. Am. Chem. Soc., 85, 1380 (1963).

properties in our laboratories, dioxygen difluoride has been observed to undergo reactions with the pentafluorides of phosphorus, arsenic and antimony yielding solid products having moderate thermal stability and considerable oxidizing power. Qualitative studies of the properties of these solids indicated that they might be structurally related to the recently reported[5, 5a] dioxygenyl salt,

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(5) N. Bartlett and D. Lohmann, J. Chem. Soc., 5253, (1962).

(5a) O_2BF_4 and O_2PF_6 were recently reported by I. J. Solomon, et. al., of the the Illinois Institute of Technology Research Foundation, Symposium on Inorganic Fluorine Chemistry, Argonne National Laboratories, Sept. 4-6, 1963.

O_2PtF_6. The results of quantitative studies of reactions with water and with nitrogen dioxide, as well as infrared and X-ray data appear to support a characterization of dioxygen difluoride-Group V pentafluoride reaction products as dioxygenyl salts of composition, O_2MF_6 (M=P, As, Sb).

DISCUSSION

The reactions of O_2F_2 with the Group V pentafluorides occur at temperatures slightly above the melting point of dioxygen difluoride (-163.5°C). After completion of the reactions, as indicated by a rapid increase in pressure and the disappearance of the orange color of dioxygen difluoride, the gaseous fraction which is not condensable at -196°C contains an excess of fluorine over oxygen.

The solid products obtained in these reactions are white at room temperature, but at -80°C or lower they develop violet-volored areas on their surfaces. They fume in moist air and react violently with water and organic solvents.

Thermal Decomposition

The products derived from arsenic and antimony pentafluorides are stable at room temperature and ordinary pressures. Rapid decomposition occurs only at temperatures above 100°C. When samples of the O_2F_2-AsF_5 or O_2F_2-SbF_5 reaction products are evacuated to 10^{-6}mm pressure, small mass peaks due to the O_2^+ are observed in the mass spectra of the vapors above the solids. The O_2^+ mass peaks increase in intensity as the samples are heated, and eventually peaks are observed which can be attributed to mass fragments derived from arsenic pentafluoride and antimony pentafluoride, respectively (Table I). Aliquots of the noncondensable (at -196°C) decomposition gas from the O_2F_2-AsF_5 product were shown by reaction with mercury to contain fluorine as well as oxygen.

The product derived from phosphorus pentafluoride decomposes rapidly at room temperature and even at -80°C undergoes slow decomposition. The decomposition gas consists of phosphorus pentafluoride, oxygen, and fluorine, the ratio of oxygen to fluorine being approximately 2:1.

Table I

Thermal Decomposition of O_2F_2-MF_5 Reaction Products

O_2F_2-AsF_5 Reaction Product		O_2F_2-SbF_5 Reaction Products	
T^oC	Observed Ions	T^oC	Observed Ions
Ambient	O_2^+	Ambient	O_2^+
40	F^+, O_2^+, AsF_n^+ (n=0 ⟶ 4)	50	O_2^+
50	F^+, O_2^+, AsF_n^+ (n=0 ⟶ 4)	125	F^+, O_2^+, SbF_3^+, SbF_4^+
75	F^+, O_2^+, AsF_n^+ (n=0 ⟶ 4)	150	F^+, O_2^+, SbF_n^+, Sb_4^+ (n=0 ⟶ 4)

The composition of the decomposition gases from the solid products suggests that their preparation and decomposition may be represented by equations 1 and 2.

$$O_2F_2 + MF_5 \longrightarrow O_2MF_6 + 1/2\ F_2 \qquad (1)$$

(M = P, As, Sb)

$$O_2MF_6 \longrightarrow O_2 + 1/2\ F_2 + MF_5 \qquad (2)$$

Reaction with Water

All of the dioxygen difluoride Group V pentafluoride reaction products evolve a mixture of oxygen and ozone when treated with water, and the resultant solutions are acidic. A quantitative study of the reaction of water with the AsF_5 product shows that the total number of moles of oxygen and ozone liberated is equivalent to the number of moles of dioxygenyl hexafluoroarsenate reacted. This result is

in agreement with the reaction shown in equation 3. Convincing chemical evidence was obtained for the existence of the hexafluoroarsenate ion in the

$$2\ O_2AsF_6 + H_2O \longrightarrow O_2 + O_3 + HAsF_6 \qquad (3)$$

residual aqueous solution. When the solution is treated with hydrogen sulfide it fails to form a precipitate of arsenic pentasulfide, but it immediately forms a white precipitate when treated with tetraphenylarsonium chloride. This behavior has been reported previously for the hexafluoroarsenate ion.[6,7]

(6) H. M. Dess and R. W. Parry, J. Am. Chem. Soc., 79, 1589(1957).

(7) H. M. Dess, Ph.D. Thesis, University of Michigan, 1959.

Reaction with Nitrogen Dioxide

The dioxygenyl compounds oxidize nitrogen dioxide to the nitronium ion, oxygen is liberated and the residual solids may be identified as nitronium salts by their infrared spectra. Quantitative determinations (carried out on the arsenic compound) of the oxygen liberated during this reaction are in agreement with the values predicted by equation 4.

$$O_2AsF_6 + NO_2 \longrightarrow O_2 + NO_2AsF_6 \qquad (4)$$

Infrared Spectra

Infrared spectra of dioxygenyl hexafluoroarsenate and of dioxygenly hexafluoroantiomate show characteristic absorptions[8,9] for the hexafluoroarsenate

(8) G A. Olah, et. al , J. Am. Chem. Soc., 84, 2733(1962).

(9) H. C. Clark and R. J. O'Brien, Proc. Chem. Soc., 113(1963).

ion at 705 cm^{-1} and the hexafluoroantiomate ion at 669 cm^{-1}, respectively.

X-Ray Diffraction Patterns

The powder diffraction spacings obtained for dioxygenyl hexafluoroarsenate (Table II) may be correlated on the basis of a cubic unit cell with a_o = 8.00 Å. The powder diffraction pattern of nitrosyl hexafluoroarsenate was photographed for comparison and it appears (Table II) that the two compounds are isomorphous. In view of the similarity in size of the nitrosyl (NO^+) and dioxygenyl (O_2^+) cations[5], this result further supports the characterization of the dioxygen difluoride-arsenic pentafluoride product as a dioxygenyl salt, O_2AsF_6.

Some difficulty was encountered in obtaining a satisfactory diffraction pattern for O_2SbF_6, most of the photographs showed only one or two lines. It is believed that the difficulty in obtaining satisfactory patterns was due to reaction of the powder samples with the glass capillary walls. The data shown in Table III are a composite of two fairly sharp patterns. The lines correlate roughly with calculated values for a cubic unit cell, a_o = 10.71 Å. The reported cell dimension for $NOSbF_6$[5] is 10.19 Å.

Table II

Diffraction Patterns of O_2AsF_6 and $NOAsF_6$

Cubic Unit Cell

$a_o = 8.00 \pm .02$ Å		O_2AsF_6		$NOAsF_6$	
h, k, l	d, Å (Calcd.)	d, Å	I/I_o (Rel.)	d, Å	I/I_o (Rel.)
111	4.62	4.60	100	4.61	100
200	4.00	3.99	100	4.00	100
220	2.83	2.83	50	2.84	40
311	2.41	2.43	10	2.43	5
222	2.31	2.32	20	2.32	20
---	---	2.10	5	---	---
400	2.00	2.01	10	2.01	5
---	---	1.93	4	---	---
331	1.83	1.85	10	1.85	10
420	1.79	1.80	20	1.80	20
422	1.63	1.64	20	1.65	20
333, 511	1.54	1.55	15	1.55	15
---	---	1.49	6	---	---
440	1.42	1.42	6	1.42	2
531	1.35	1.36	10	1.36	5
442, 600	1.33	1.34	10	1.34	5
620	1.27	1.27	5	1.28	2
---	---	---	---	1.25	2
533	1.22	---	---	1.24	2

Table III

Diffraction Pattern of O_2SbF_6

Cubic Unit Cell

$a_o = 10.71 \pm 0.15$ Å

h, k, l	d, Å (Calcd.)	O_2SbF_6 d, Å	O_2SbF_6 I/I_o (Rel.)
---	---	5.45	20
200	5.35	5.33	20
---	---	5.11	15
210	4.79	4.87	8
---	---	4.11	20
220	3.84	3.84	100
300, 221	3.52	3.53	35
310	3.39	3.39	5
311	3.23	3.23	10
222	3.09	3.16	15
321	2.86	2.80	8
400	2.68	2.68	12
410, 322	2.60	2.61	5
331	2.46	2.43	10
422	2.19	2.24	5
500, 430	2.14	2.13	5
511, 333	2.06	2.05	10
440	1.89	1.84	10
522, 441	1.82	1.81	10
620	1.69	1.70	10
621, 540, 443	1.67	1.67	5
631	1.58	1.59	5
711, 551	1.50	1.51	5

EXPERIMENTAL

A Bendix Time-of-Flight Mass Spectrometer (Model 12-101) was used to identify gaseous products obtained in the thermal decomposition studies and from reactions of the dioxygenyl salts with water and NO_2. Infrared spectra were obtained on sodium fluoride pellets using a Perkin Elmer Model 21 Spectrophotometer. Positive identification of the nitronium ion by its absorption at 2350 cm^{-1} was accomplished by scanning fluorocarbon mills of the O_2MF_6-NO_2 reaction products from 1 to 7 microns. Powder diffraction patterns were photographed with CuK radiation from a nickel filter. The X-ray samples were sealed under nitrogen in Pyrex capillaries.

Oxygen, fluorine, and nitrogen dioxide were purchased from the Matheson Company, Inc., East Rutherford, N.J. Phosphorus pentafluoride, arsenic pentafluoride, antimony pentafluoride, and nitrosyl hexafluoroarsenate were purchased from the Ozark-Mahoning Co., Tulsa, Oklahoma.

Preparation of Dioxygenyl Salts

(a) O_2PF_6 and O_2AsF_6 - The reactions of dioxygen difluoride with phosphorus pentafluoride and arsenic pentafluoride were conducted in all glass vacuum apparatus. Approximately one millimole of phosphorus pentafluoride or arsenic pentafluoride was distilled into an evacuated U-shaped trap at -196°C. Copper electrodes had been sealed into both legs of the trap so that it could be used as

a discharge tube. Excess dioxygen difluoride was generated at -196°C according to the procedure of Kirshenbaum and Grosse[10] and was condensedin the legs of

(10) A. D. Kirshenbaum and A. V. Grosse, J. Am. Chem. Soc., 81, 1277 (1959).

the trap as an orange solid. As the liquid nitrogen (-196°C) bath was lowered, the dioxygen difluoride melted and flowed to the bottom of the trap where it came into contact with arsenic pentafluoride or phosphorus pentafluoride. After the orange color of the dioxygen difluoride had been discharged due to thermal decomposition, as well as reaction with the Group V pentafluoride, the trap was again cooled to -196°C, and the gas present at that temperature was sampled for fluorine analysis by absorption in mercury. The solid products were then pumped at -80°C for one hour, and, in the case of the arsenic pentafluoride product, at room temperature for two additional hours. The products were white solids at room temperature but developed violet colored areas on their surfaces when cooled to -80°C. O_2PF_6 was stored in the reactor at -80°C. O_2AsF_6 was sufficiently stable at room temperature to permit the transfer of the solid, in a dry box, to a Kel-F sample vial.

(b) O_2SbF_6 - The preparation of O_2SbF_6 was carried out in a vacuum apparatus constructed of Kel-F and brass. Antimony pentafluoride was weighed into a Kel-F tube in a dry atmosphere box. The tube was attached to the

vacuum system at a distance of about three inches from the O_2F_2 generator, which was a Kel-F U-trap with copper electrodes. Excess dioxygen difluoride was generated at -196°C, warmed to -80°C and vacuum distilled into the tube containing the solid antimony pentafluoride at -196°C. The reagents were allowed to mix by replacing the liquid nitrogen bath with a Dry Ice-Trichlor bath (-80°C), so that the dioxygen difluoride could melt and flow onto the solid antimony pentafluoride. The O_2SbF_6 was pumped for several hours and then stored under dry nitrogen at room temperature.

Analytical Determinations - Arsenic, antimony, and fluorine were determined on solutions obtained by the reaction of weighed samples of O_2AsF_6 and O_2SbF_6 with water as described below. In the case of O_2AsF_6, perchloric acid was added to the solutions and they were boiled in order to break up the hexafluoroarsenate complex.[7] The solutions were distilled until fumes of perchloric acid were observed in the distillation flask. Fluorine was determined in the distillates by titration with thorium nitrate solution. Arsenic was determined gravimetrically on the pot residues as the pentasulfide.

Anal. Calcd. for O_2AsF_6: As, 33.91, F, 51.60.

Found : As, 33.86, F, 51.11.

The hexafluoroantimonate complex could be destroyed simply by adding H_2S to an aliquot of the solution obtained by the reaction of O_2SbF_6 with water.

The precipitate was dried at 280°C and weighed as Sb_2S_3. Fluoride was determined on a separate aliquot by titrating with thorium nitrate.

Calcd. for O_2SbF_6: Sb, 45.47; F, 42.59.

Found : Sb, 46.05; F, 39.22.

Reaction with Water - All three solid O_2F_2-Group V pentafluoride reaction products liberated a mixture of oxygen and ozone when allowed to react with water. Samples of O_2AsF_6 were weighed under dry nitrogen in a 50 ml round bottom Pyrex flask. The flask was attached to the vacuum system of calibrated volume, water was distilled into the flask at -196°C, and the flask was then allowed to warm to room temperature, where a vigorous reaction occurred. The total pressure was measured and a sample of the gas evolved by the reaction was identified as a mixture of oxygen and ozone by mass spectroscopy. The results of two determinations were as follows:

Wt. O_2AsF_6	Total O_2 and O_3, Found	Total O_2 and O_3, Calcd. by eq. 3
0.1728 g	0.790 mmole	0.785 mmole
0.1608 g	0 701 mmole	0.729 mmole

Reaction with Nitrogen Dioxide

(a) O_2PF_6 - PF_5 (1.31 mmoles) was allowed to react with excess O_2F_2 as described above. The reactor was warmed to -80°C and evacuated through a trap at -196°C. The gas (0.705 mmole) condensed in the -196°C trap was

identified by mass spectroscopy as a mixture of POF_3, SiF_4, and PF_5. The reactor was then cooled to -196°C, and approximately two mmoles of NO_2 was condensed onto the solid. A carbon tetrachloride slush bath (-23°C) was placed under the reactor for approximately three hours and then replaced by a -196°C bath. The residual gas was transferred to a bulb of known volume by means of a Toepler pump. The quantity of gas thus removed from the reactor was found to be 1.05 mmoles. It was identified as pure oxygen by mass spectroscopy. The solid residue was removed from the reactor in a dry box in order to obtain an infrared spectrum. It was identified as NO_2FP_6 by absorptions at 2350 cm^{-1} (NO_2^+) and at 837 cm^{-1} (PF_6^-).

(b) O_2AsF_6 - Weighed samples of O_2AsF_6 were allowed to react with excess NO_2 by a procedure identical to that used to carry out the reaction with water. The noncondensable (at -196°C) gas produced by the reaction was measured in a calibrated bulb and identified as oxygen by mass spectroscopy. The results of two determinations were as follows:

Run No.	Wt O_2AsF_6	O_2, Found	O_2, Calcd. (eq. 4)	Wt NO_2AsF_6 Found	Wt NO_2AsF_6, Calcd. (eq. 4)
1	0.2160 g	1.08 mmoles	0.970 mmole	---	---
2	0.1926 g	0.897 mmole	0.872 mmole	0.2043 g	0.2048 g

Thermal Decomposition

(a) O_2PF_6 - The product obtained by the reaction of PF_5 with O_2F_2 decomposed slowly on standing at -80°C in vacuo. After a 24 hour period at -80°C, the trap containing the O_2PF_6 was cooled to -196°C. The noncondensable gas at -196°C was pumped by means of a Toepler pump, through a U-trap containing sodium chloride at 100°C Chlorine was produced by reaction of the sodium chloride with the fluorine present in the decomposition gas. The chlorine was condensed in a second U-trap at -196°C. The oxygen in the decomposition gas passed through both traps and was transferred into a bulb of known volume. The quantity of oxygen measured was 0.116 mmole and the quantity of chlorine (equivalent to the initial fluorine) found was 0.063 mmole. The oxygen to fluorine ratio in the decomposition gas was therefore 1.85/1.00.

(b) O_2AsF_6 - Determination of the oxygen fluorine ratio in the noncondensable decomposition gas from pyrolyzed samples of O_2AsF_6 consistently gave high results (theoretical $O_2/F_2 = 2$). This was due to the consumption of fluorine by reaction with the walls of the pyrolysis and gas measuring apparatus at the temperatures required to induce rapid decomposition (130°-180°C). The pyrolysis tubes were constructed from 13 mm diameter copper or Teflon tubing fitted by means of a Swagelock connection to a Monel valve and ball joint. Samples of O_2AsF_6 (30-100 mg) were loaded into the tubes under dry nitrogen, the Swagelock connection was tightened and the tubes were attached to a Pyrex vacuum system and evacuated. Included in the Pyrex

vacuum system were a U-trap, a manometer having a 1 cm protective layer of Fluorolube oil on the surface of the mercury, and a tube of known volume into which mercury could be admitted in order to absorb fluorine. The pyrolysis tubes were heated for several hours at approximately 180°C with the valves open to the U-trap (at -196°C) and manometer. Aliquots of the noncondensable decomposition gas were admitted to the calibrated tube where they were shaken over mercury to absorb the fluorine. The pressure of residual gas was measured and it was identified as oxygen by mass spectroscopy. The results obtained in three typical runs are as follows:

Run	Noncondensable Aliquot (mmole)	O_2, Found (mmole)	F_2, by Difference (mmole)	O_2/F_2
1	0.060	0.047	0.013	3.6
2	0.275	0.205	0.070	2.9
3	0.112	0.085	0.027	3.1

Acknowledgement- We wish to acknowledge the contribution of Messrs. R. N. Storey, E. Egbert, D. Yee and A. Fremmer in performing instrumental and wet chemical analysis.

III. APPENDIX - INORGANIC CHEMISTRY OF THE OXYGEN SUBFLUORIDES

A. INTRODUCTION

The studies discussed in this section of the report were initiated during the past year and are still in progress. Most of the results presented herein were obtained in experiments in which either no reaction occurred or the course of reaction is not fully understood at present.

B. CHEMISTRY OF DIOXYGENYL COMPOUNDS

In Section II of this report a description is given of two reactions of dioxygenyl salts that were used in their characterization, namely, their reactions with water and nitrogen dioxide. Other reactions of dioxygenyl salts (principally with O_2AsF_6) with a variety of inorganic and some organic reagents were also briefly investigated. These studies had as their main objective the discovery of a suitable solvent in which the chemistry of the dioxygenyl ion could be observed; an additional objective was to detect formation of previously unreported compounds. Much of the data to be reported as a result of these studies are preliminary and inconclusive and several reactions of unusual interest will be studied further.

1. Reactions of Dioxygenyl Salts with Inorganic Reagents

a. Reaction of O_2AsF_6 with Cl_2

The reaction of Cl_2 with O_2AsF_6 was studied in a glass system by condensing Cl_2 onto O_2AsF_6 powder at $-196^{\circ}C$. As in the case of the reaction of Cl_2 with O_2F_2 (Ref 1), a violet colored intermediate compound forms at or near $-196^{\circ}C$. The violet compound is quite stable at $-78^{\circ}C$ and may be pumped until all materials volatile at $-78^{\circ}C$ have been removed. As the violet compound is warmed to room temperature, it undergoes a color change from violet to orange, to yellow and finally, at room temperature only a trace of solid (white) remains. The gas phase at room temperature consists of O_2, Cl_2, ClO_2F, and SiF_4. It is believed that these are present due to decomposition and reaction of the initial products with glass and that the most probable reaction is as shown in equation 1.

$$O_2AsF_6 + Cl_2 \xrightarrow{-78^\circ C} \text{a violet complex} \xrightarrow{rt} ClO_2 + ClF + AsF_5 \quad (1)$$

b. Reaction of O_2SbF_6 with ClF_3

When O_2SbF_6 is treated with ClF_3 at its melting point, there is an immediate reaction which results in the liberation of oxygen and fluorine. It was thought at first that the reaction proceeds as shown in equation 2, but data obtained in

$$O_2SbF_5 + ClF_3 \xrightarrow{?} ClF_2SbF_6 + O_2 + 1/2\ F_2 \quad (2)$$

in several runs are not in agreement with the stoichiometry required by equation 3. The results, summarized in Table I, show that the oxygen liberated during the reactions with ClF_3 was only 13 to 25% of the calculated dioxygenyl content of the solid, and that the O_2/F_2 ratio in the evolved gas was considerably greater than the 2:1 ratio required by equation 2. Therefore, the question of whether O_2SbF_6 is soluble or compatible with ClF_3 has not been resolved and this system must be examined further.

TABLE I

REACTION OF O_2SbF_6 WITH ClF_3

Exp. No	Salt	% of Theoretical O_2 Obtained	% of Theoretical F_2 Obtained	Composition of Gas, % O_2
168458	O_2SbF_6	12.8	8.6	91.4
168452	O_2SbF_6	15.5	8.1	91.9
168463	O_2SbF_6	24.8	10.0	83.2

c. Reaction of O_2AsF_6 with AsF_5

O_2AsF_6 dissolved in AsF_5 (mp - 5.9°C) at room temperature with vigorous gas evolution. The gaseous products identified were O_2 and AsF_5 and there was no solid residue upon distilling the excess liquid AsF_5. The reaction observed is most probably that shown in equation 3.

$$2\ O_2AsF_6 + AsF_5 \longrightarrow 2\ O_2 + 3AsF_5 \quad (3)$$

d. Reaction of O_2AsF_3 with BF_3

O_2AsF_3 was insoluble in BF_3 at its melting point (-126°C) and there was no evidence of reaction between the reagents.

e. Reaction of O_2AsF_3 with SbF_5

Excess SbF_5 (mp 7°C) was distilled onto a sample of O_2AsF_3 in a glass apparatus. At room temperature, there appeared to be a violet colored solution present, but a good portion of the O_2AsF_3 remained undissolved and floated on the surface of the SbF_5 (d = 2 99 g/ml). Slow gas evolution was observed in the liquid over a period of a week. Since this gas was almost completely condensable at -196°C, it was thought to be AsF_5 (equation 4). However infrared analysis of the gas phase showed only SiF_4 and a trace of BF_3, both due evidently to a reaction with the glass Some white solid remained after removal of the

$$O_2AsF_3 + SbF_5 \longrightarrow O_2SbF_3 + AsF_5 \qquad (4)$$

SbF_5, but it was mixed with a large amount of yellow solid (Sb_2O_3) and no attempt was made to identify it. Further studies on the O_2AsF_3-SbF_5 system will be carried out in a Kel-F apparatus

f. Reaction of O_2AsF_3 with Hydrogen Fluoride

O_2AsF_3 forms a violet solution in HF at -78°C which appears to be stable. However, if the solution is warmed to above -50°C it rapidly becomes colorless and evolves a noncondensable gas. In several runs with weighed samples of O_2AsF_3 the noncondensable gas has been carefully measured and analyzed. In each case it has been found to be virtually pure oxygen, the quantities being equivalent to the calculated oxygen content of O_2AsF_3. The absence of fluorine in the decomposition gas (equation 5) remains a mystery. There is the possibility that the fluorine reacts with the reactor walls (Kel F), because some volatile C-F compounds were detected in the vapor phase over the liquid HF at 80°C after removal of the oxygen at -196°C Another possibility is that some as yet undetected impurity in the HF undergoes fluorination. Although the studies to date indicate that reactions of O_2AsF_3 may be carried out in HF at temperatures in the vicinity of 78°C, further study of the behavior of the O_2AsF_3 HF system at higher temperatures must be undertaken in order to define the nature of the observed decomposition reaction.

$$O_2AsF_3 \longrightarrow O_2 + 1/2\ F_2 + AsF_3 \qquad (5)$$

g. Reaction of O_2AsF_6 with NO

Nitric oxide reacts quite readily with O_2AsF_6 at low temperatures. NO_2 is liberated (equations 6 and 7) and nitrosyl hexafluoroarsenate is formed.

$$NO + O_2AsF_6 \longrightarrow O_2 + NOAsF_6 \quad (6)$$

$$1/2\ O_2 + NO \longrightarrow NO_2 \quad (7)$$

h. Reaction of O_2AsF_6 with NO_2ClO_4

O_2AsF_6 and NO_2ClO_4 do not react when mixed in the solid state but when HF is distilled onto the mixed solids at -80°C, gas is evolved and an orange solution forms. Gases identified above the HF solution were O_2, ClO_3F, and AsF_5. After removal of the HF by pumping at -50°C, a solid residue was obtained. A sample of this solid was examined in the infrared as an NaF pellet and it showed an unidentified absorption at 5.45μ, as well as absorptions attributable to NO_3^-, ClO_4^-, and AsF_6^- anions.

i. Reaction of O_2AsF_6 with SO_2Cl_2

O_2AsF_6 forms an unstable violet solution in SO_2Cl_2 at room temperature. The solution decolorizes rapidly with gassing, liberating O_2, SO_2ClF, and SO_2F_2. Previously known methods of fluorinating SO_2Cl_2 required drastic conditions of temperature and pressure. It is possible that the powerful fluorinating ability of O_2AsF_6 is due to the transient formation of O_2F shown in equation 8.

$$O_2AsF_6 \longrightarrow \left[O_2F\right] + AsF_5 \longrightarrow O_2 + \cdot F + AsF_5 \quad (8)$$

2. Reactions of Dioxygenyl Salts with Compounds of Carbon

As a part of our exploratory studies of the properties of O_2MF_6 compounds, reactions with unsaturated hydrocarbon and fluorocarbons were examined.

a. Reaction of O_2MF_6 Salts with CF_2CFCl

It was found that both O_2AsF_6 and O_2SbF_6 behave in a comparable fashion with $F_2C{=}CFCl$. Products obtained upon reacting either dioxygenyl salt with $F_2C{=}CFCl$ at room temperature were: COF_2, $COClF$, CF_2ClCF_2Cl, CF_3CFCl_2, and CF_3CFO.

b. Reaction of O_2AsF_6 with C_2H_4

The reaction of O_2AsF_6 with ethylene resulted in an ignition at about room temperature. Reaction products were not identified because the ignition and pressure rise caused a leak in the system.

c. Reaction of O_2AsF_6 with CH_3CN

Acetonitrile was distilled onto a sample of O_2AsF_6 at 196°C As the reactant mixture was warmed from -196°C, a delicate pink to orange color was noted on the dioxygenyl solid There was slight fuming of the mixture near room temperature and the solid completely dissolved forming an amber colored solution. Analysis of volatile products by mass spectroscopy showed the following to have been present O_2, CO_2 or N_2O, $C_2F_4H_2$, CF_4, H_3CF, H_2CF_2, CH_3CF_2H, CH_2FCFH_2, and SiF_4 (from the glass reactor). In addition, absorptions for the following functional groups appeared in the infrared spectrum of the vapor phase a carboxylic acid, an alkyl nitrite, an alkyl nitrate, and an aliphatic alcohol. Analysis of the amber residue left behind after distilling off all of the volatile products showed that a compound containing the AsF_6^- anion was present. Complete analysis of this residue has not been completed.

3. Reactions of O_2F_2

Additional studies of O_2F_2 chemistry during the past year consisted of:

(a) Attempts to prepare dioxygenyl salts of anions other than the univalent hexafluoroanions of the Group V elements

(b) Attempts to elucidate the composition and structure of low temperature violet addition compounds of O_2F_2 and Cl_2 or chlorine compounds

a Reaction of O_2F_2 with Xe

Because of the current interest in compounds of the noble gases, it was decided to attempt the preparation of dioxygenyl derivatives of XeF_4 or XeF_2 as shown in equation 9 The reaction was initially conducted in a glass system.

$$O_2F_2 \text{ (excess)} + Xe \xrightarrow[160^\circ C]{?} (O_2)_m XeF_n \qquad (9)$$

Xe was condensed into the bottom of a U-shaped discharge tube at -196°C and O_2F_2 was generated on the walls of the tube. The tube was warmed up to the melting point of O_2F_2 (-160°C) where it flowed onto the Xe. The system was warmed to -80°C and pumped until it exhibited no vapor pressure. Upon removal of the -80°C bath, a white solid was observed in the tube, which built up a decomposition pressure as it warmed to room temperature. The decomposition gases consisted of O_2, SiF_4, and Xe.

The reaction was repeated in a Kel-F apparatus but the solid appeared to be as unstable in Kel-F as it was in glass. Because of the thermal instability of the Xe-containing solid no further attempts were made to characterize it.

b. Reaction of O_2F_2 with $SnCl_4$

The possibility of forming a dioxygenyl salt of a bivalent cation was tested by reacting $SnCl_4$ with excess O_2F_2 (equation 10). A reaction giving rise to a violet addition compound took place at the melting point of O_2F_2. This behavior

$$O_2F_2 \text{ (excess)} + SnCl_4 \xrightarrow{?} (O_2)_2SnF_6 + 2Cl_2 \qquad (10)$$

is characteristic for chlorine-containing compounds in the presence of O_2F_2. The violet solid decomposed on warming to room temperature and chlorine was found to be the major condensable gaseous decomposition product. A white solid remained at room temperature which could not be identified by its x-ray pattern. The solid gave off only a trace of oxygen and ozone upon treatment with water.

In the light of our observation of the decomposition of O_2AsF_6 by Cl_2 (Section 1, Reaction of O_2AsF_6 with Cl_2), it is not surprising that a significant amount of dioxygenyl salt was not isolated in this reaction. In future attempts to prepare $(O_2)_2SnF_6$, SnF_4 will be used as an initial reagent.

c. Reaction of O_2F_2 with POF_3

O_2F_2 and POF_3 reacted at -160°C to produce a solid which slowly evolved O_2 at -78°C. At room temperature, the solid disappeared rapidly and POF_3, and

O_2 were detected in the decomposition gases. No further attempts have been made to characterize this unstable product.

d. Reaction of O_2F_2 with Cl_2

Studies of the reaction of O_2F_2 with Cl_2 have been reported by us for the past two years (Ref 2) The reaction yields a violet solid product at -160°C which is stable to approximately -78°C. This behavior has also been observed with many compounds of chlorine, such as CCl_4, BCl_3, $ClNF_2$, ClF, $SiCl_4$, and HCl.

A recent publication by Streng and Grosse (Ref 3) presents analytical data which show that the violet compound obtained from ClF and O_2F_2 is a 1:1 addition product. $ClF.O_2F_2$ decomposes above -78°C to O_2 and ClF_3. It is further pointed out in this paper that the violet compounds observed when Cl_2 or HCl react with O_2F_2 are identical in composition to the $ClF-O_2F_2$ product (equations 11 through 13).

$$ClF + O_2F_2 \longrightarrow O_2F_2{\cdot}ClF \longrightarrow O_2 + ClF_3 \qquad (11)$$

$$Cl_2 + O_2F_2 \longrightarrow 2ClF + O_2 \xrightarrow{O_2F_2} O_2F_2\,ClF \longrightarrow O_2 + ClF_3 \qquad (12)$$

$$HCl + O_2F_2 \longrightarrow ClF + HF + O_2 \xrightarrow{O_2F_2} O_2F_2{\cdot}ClF \longrightarrow O_2 + ClF_3 \qquad (13)$$

In our investigations of the nature of the violet addition compounds we have not been able to obtain the clear cut decomposition reactions shown in equations 11, 12 and 13 When the $Cl_2-O_2F_2$ product decomposes its decomposition gas contains O_2, F_2, Cl_2, ClO_2, ClO_2F, ClO_3F, and in glass systems, SiF_4. We have never observed ClF_3 although we have used Kel-F apparatus as well as glass. Because of the complexity of the decomposition products from the violet solid we have not been able to obtain reproducible analyses and the questions of its composition and structure remain unresolved.

4. Low Temperature Infrared Studies

A study of the infrared spectra of O_2F_2 and its reaction products at low temperatures was initiated during the final quarter. It is believed that this approach will eventually prove to be quite helpful in elucidating the structure

and composition of reaction products obtained from O_2F_2. This is especially true in cases, such as the Cl_2-O_2F_2 reaction, where the initial reaction product is thermally unstable and its thermal decomposition leads to a complex mixture of products.

The infrared cell used in these studies is shown in Figure 1. The body of the cell was constructed of Pyrex and the large outer windows of NaCl. Samples to be scanned are frozen out on the copper cube in the center of the cell, one face of which is fitted with an AgCl window. The copper tube is cooled to any desired temperature by filling the inner member of the large standard taper joint with refrigerant.

a. Spectrum of O_2F_2

Spectra from 2-15μ obtained in two separate runs with solid O_2F_2 are shown in Figures 2 and 2A. These spectra show absorptions in the same general areas but the spectrum in Figure 2A has greater definition, which may be due to a difference in sample thickness. The spectra shown here (Figures 2 and 2A) are also quite similar to a low temperature spectrum of O_2F_2 reported by I.I.T. Research Foundation (Ref 4). Again, there are minor differences which can only be resolved by further study of the effect of film thickness, temperature, and the presence of minor impurities (CO_2, COF_2, CF_4, HF, etc.) on the appearance of the absorption bands. Until these questions are resolved, it is pointless to attempt making bond assignments to the observed absorptions.

b. Spectrum of the Violet Cl_2-O_2F_2 Product

Chlorine was condensed on a layer of O_2F_2 at the surface of the AgCl window (Figure 1) The violet complex was formed by allowing the cell to warm to approximately -160°C. Upon observing the appearance of the violet addition compound on the window of the cell, the temperature was returned to -196°C and the spectrum shown in Figure 3 was obtained. The absorption at 1530 cm^{-1} (6.5μ) may be significant, since it has been reported that Cl-F has an overtone band at 1535 cm^{-1} (Ref 5) This absorption is absent in the spectrum of O_2F_2 shown in Figure 2 and in the spectrum of O_2F_2 reported by I.I.T. Research Foundation (Ref 4). However, a similar band is observed at 1525 cm^{-1} in Figure 2A, a spectrum which also was obtained with a film of solid O_2F_2. The possibility is being investigated that the bond at 1525 cm^{-1} in the latter spectrum (Figure 2A) is due to attack of the AgCl window. The infrared active products appearing in the cell when the complex was warmed above -78°C were: ClO_2, ClO_2F, SiF_4, and CF_4.

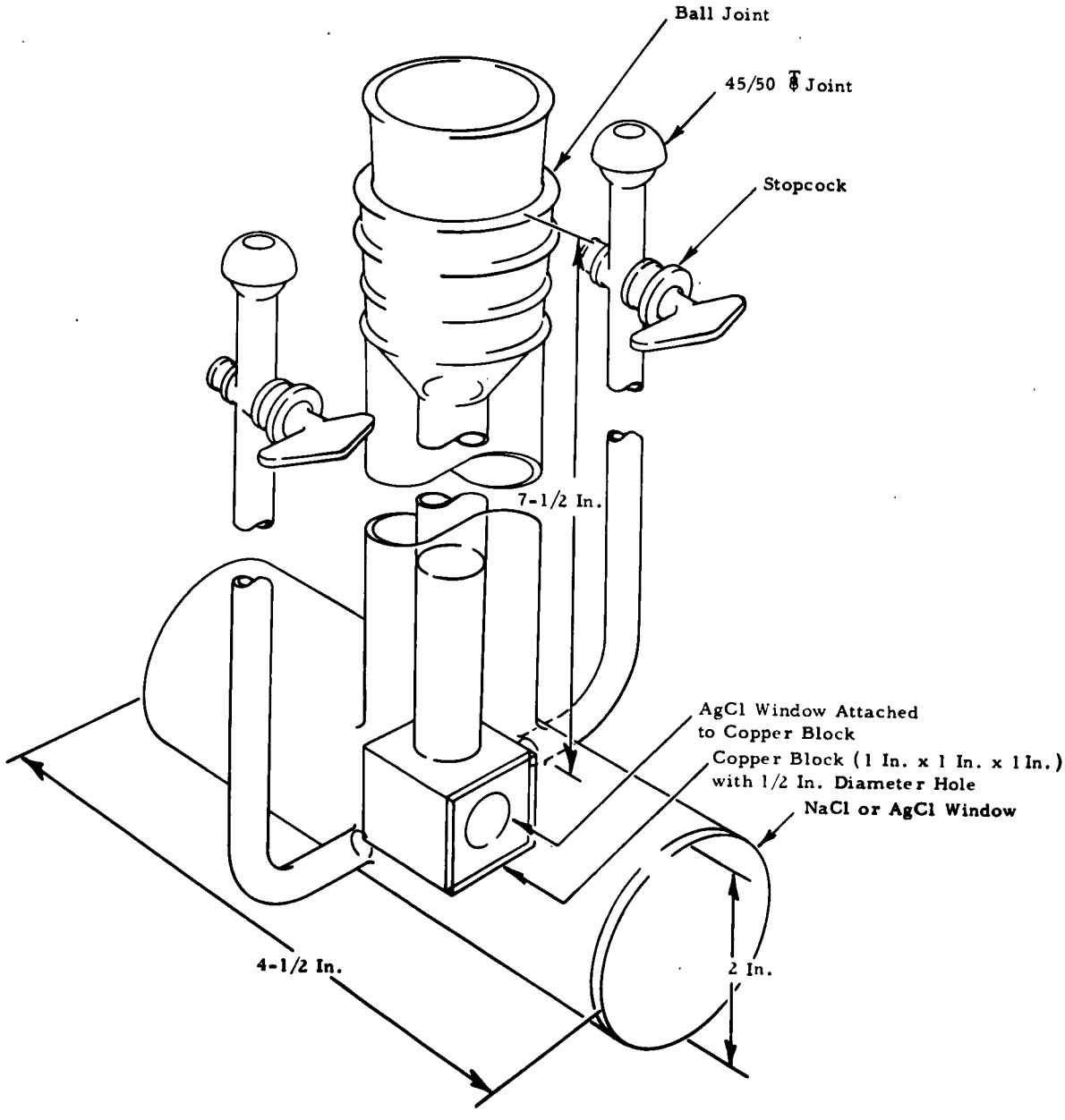

Figure 1. Diagram of Low Temperature Infrared Cell

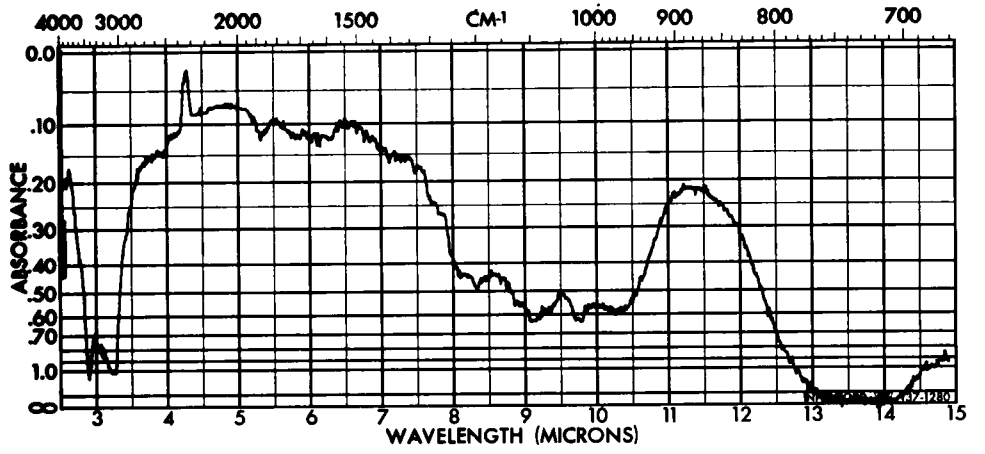

Figure 2. Infrared Spectrum of O_2F_2 Film on AgCl at -196°C

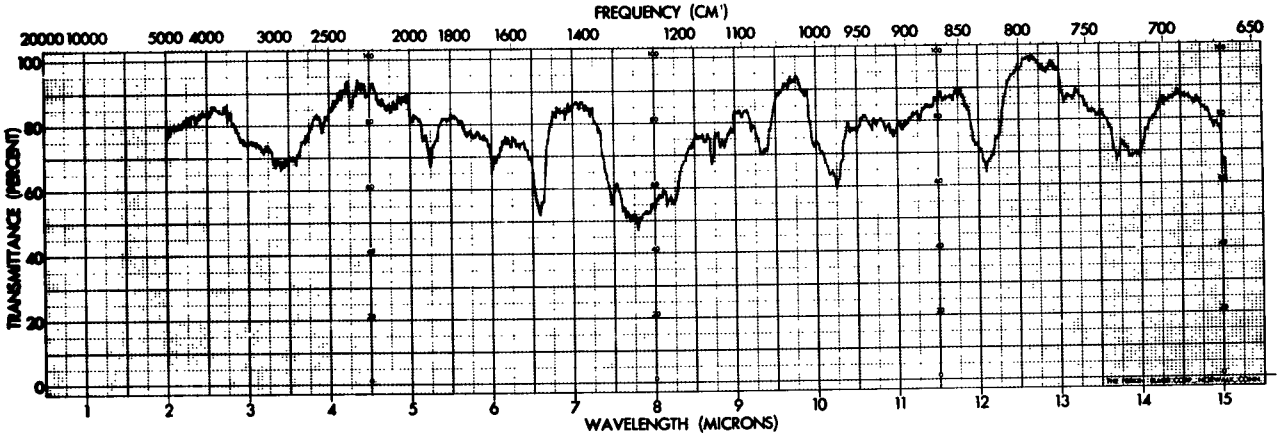

Figure 2A. Infrared Spectrum of O_2F_2 Film on AgCl at -196°C

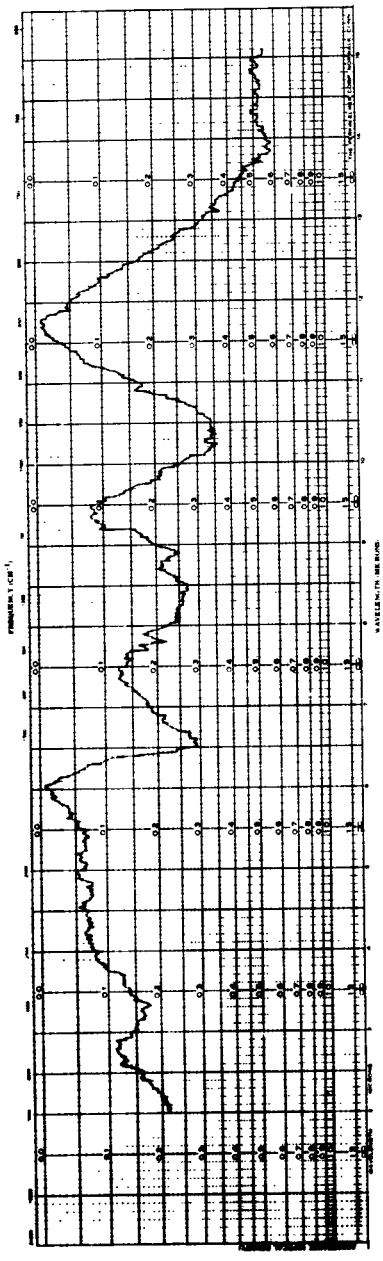

Figure 3. Infrared Spectrum of Violet Cl_2-O_2F_2 Addition Product at -196°C

c. Spectrum of the Violet $HCl \cdot O_2F_2$ Complex

The formation of a violet complex between HCl and O_2F_2 was also studied by means of infrared spectroscopy. The results of this exploratory run are shown in Figures 4 and 5. Figure 4 shows the spectrum obtained after condensing HCl onto a film of O_2F_2 at $-196^{\circ}C$. The spectrum appears to be essentially that of O_2F_2 (Figure 2 and Ref 4) with diminshed band resoltuion (again, probably due to differences in film thickness). Figure 4 is the spectrum obtained after forming the violet addition compound of HCl and O_2F_2. It is quite similar to the $Cl_2 \cdot O_2F_2$ spectrum shown in Figure 3 and shows the sharp absorption at 1530 cm^{-1} which is possibly indicative of Cl·F bonding.

Upon raising the temperature of the cell in this run to above $-78^{\circ}C$, a pressure surge occurred that cracked the outer NaCl windows.

The bonding in the O_2F_2 complexes with chlorine containing materials cannot be unequivocally established from the rather broad absorptions obtained in these studies to date. However, it is believed that refinement of our technique for obtaining these spectra, as well as extension of the spectral region to 25μ, will enable us to make bond assignments by comparison with spectra of known compounds. For example, on the basis of an infrared study of ClO_3F and assuming C_{3v} symmetry, the following band assignments have been reported (Ref 6).

Absorption (cm^{-1})	Assignment
1061	Cl O stretch
715	Cl F stretch
1315	Cl O stretch

In addition Jones et al (Ref 5) have reported an overtone band for ClF at 1535 cm^{-1}. It is possible that absorptions observed in the spectra of O_2F_2 complexes with Cl and HCl are indicative of the following bonding

Absorption (cm^{-1})	Bond
1530	Cl F
1250 1100	Cl O
1050 870	Cl·O
750 650	Cl F

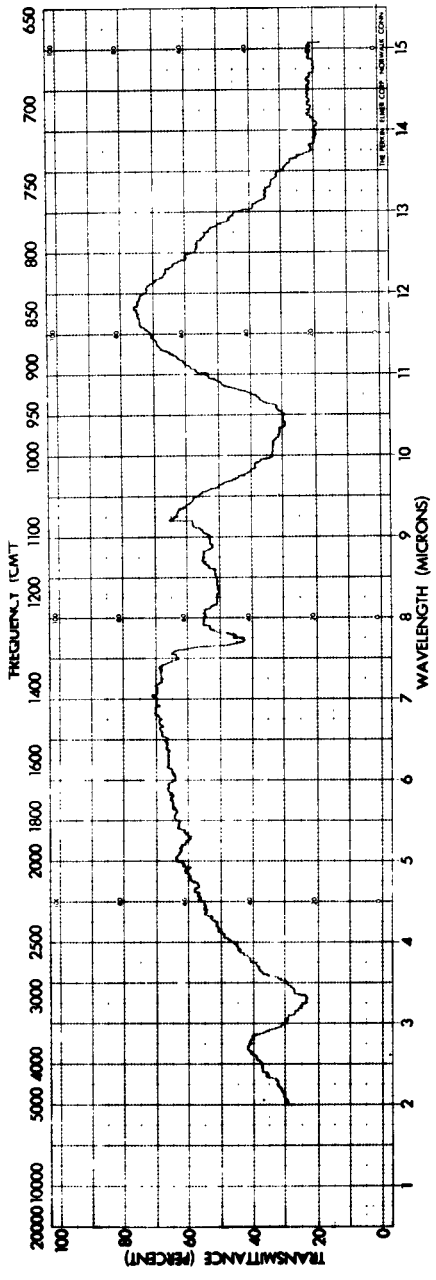

Figure 4. Infrared Spectrum of $HCl-O_2F_2$ Mixture at -196°C

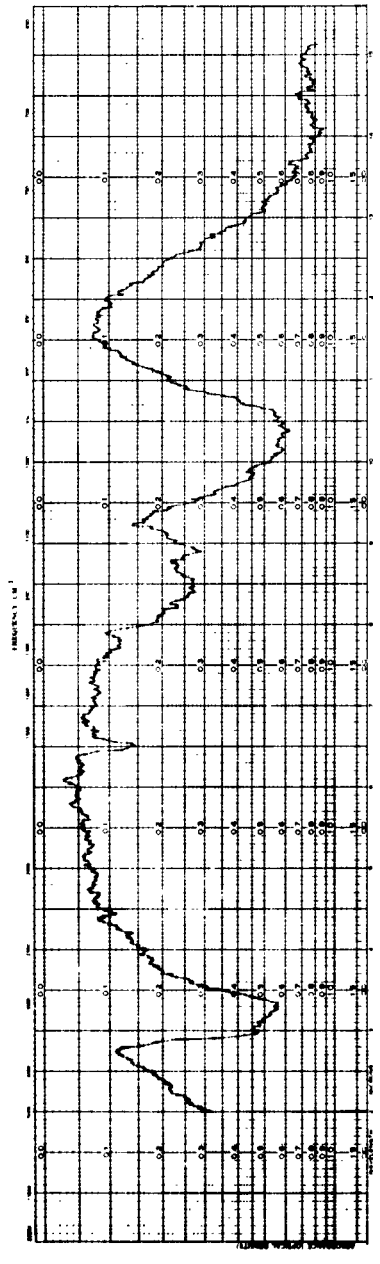

Figure 5. Infrared Spectrum of Violet HCl-O_2F_2 Addition Product at -196°C

The fact that the complexes yield ClO_2, ClO_2F and ClO_3F upon decomposition gives some substance to these assignments. It must be pointed out, however, that O_2F_2 also has absorption bands in some of the same regions (Figures 2 and 2A) as the complexes.

d. Low Temperature Spectrum of O_2AsF_6

An effort was made to obtain a spectrum of O_2AsF_6 as a film on AgCl by allowing AsF_5 and O_2F_2 to react on the cell windows at -196°C. O_2AsF_5 is stable at room temperature, but in order to obtain its spectrum it must be handled outside the vacuum apparatus and mixed with materials, such as KBr or NaF, in order to make a pellet. It was thought that the low temperature film technique would more readily yield a spectrum of the pure compound. The spectrum obtained is shown in Figure 6. It shows an absorption in the 700 cm^{-1} region which may be attributed to AsF_6^-, but unlike the spectrum reported for O_2AsF_6 that was obtained as a KBr pellet (Ref 1), it shows absorptions at higher frequencies. In reporting the KBr pellet spectrum it was pointed out (Ref 1) that a reaction had occurred on mixing the KBr and O_2AsF_6. Therefore, it is likely that the spectrum obtained in this case is that of $KAsF_6$. It is interesting to note that a spectrum of O_2AsF_6 obtained at room temperature as an NaF pellet (Figure 7) is almost identical to that obtained by the low temperature film technique.

5. Experimental

The experimental techniques utilized in the preparation of O_2F_2, in studying reactions of O_2F_2, and in studies of the chemistry of dioxygenyl salts have been described adequately in Part I of this report, as well as in the quarterly reports published during the past year (Ref 7).

Low temperature infrared studies were carried out with the cell shown in Figure 1. This was attached by a ball joint connection downstream from a U-shaped discharge tube in which O_2F_2 was generated. The copper block and internal AgCl window were cooled to -196°C by filling the inner member of the standard taper joint with liquid nitrogen. Films of O_2F_2 were formed on the cell window by distilling O_2F_2 from the generator (at -78°C) to the infrared cell. The system was constantly pumped to remove any O_2 and F_2 arising from the thermal decomposition of O_2F_2. In order to minimize loss of O_2F_2 during the transfer process, the lines connecting the generator to the infrared cell were cooled by wrapping with Pyrex wool and soaking the wool with liquid nitrogen.

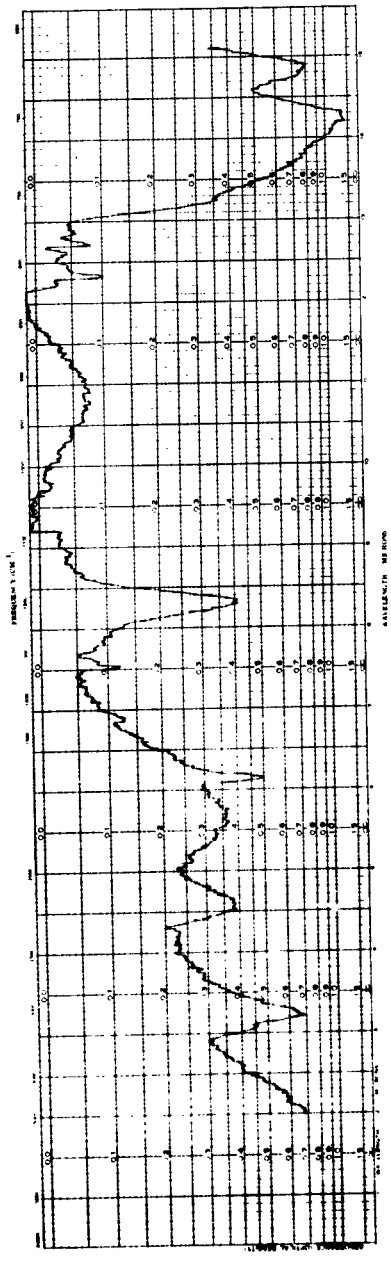

Figure 6. Infrared Spectrum of O_2AsF_6 Film on AgCl Window at -196°C

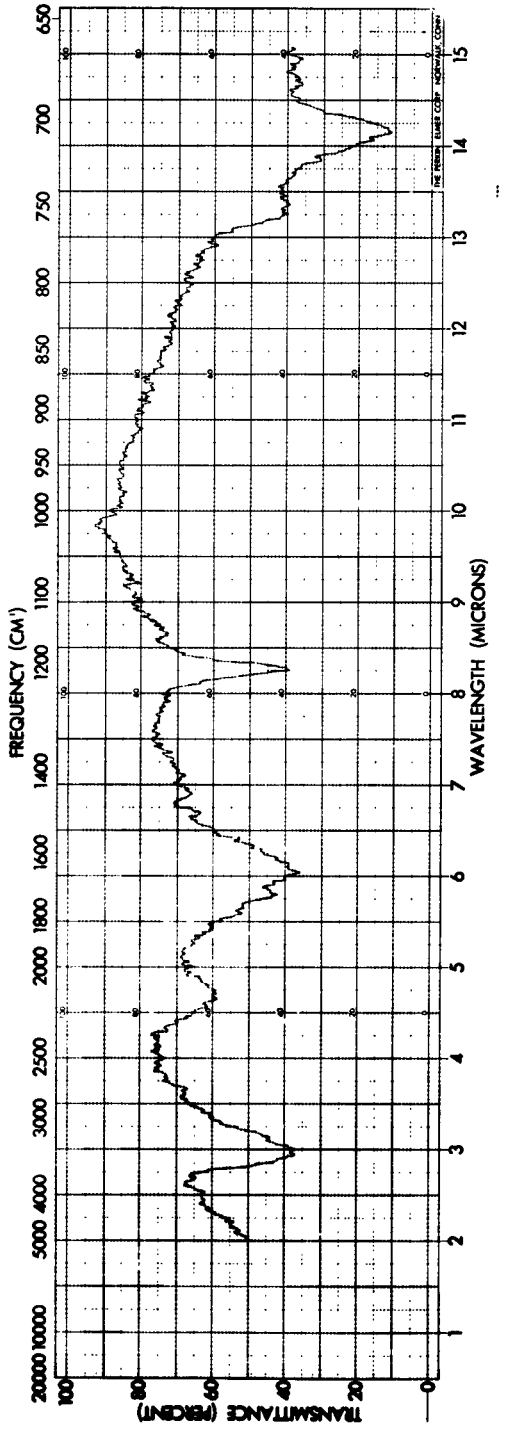

Figure 7. Infrared Spectrum of O_2AsF_6 (NaF Pellet)

The violet complexes of Cl_2 and O_2F_2 and of HCl and O_2F_2 were obtained by allowing thin films of the reagents condensed on the AgCl window at -196°C to warm by removing the liquid nitrogen from the inner joint (Figure 1). As soon as the violet color of the reaction product was observed, the window was cooled to -196°C and the spectrum was scanned.

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Section V

RMD Project 5031

INVESTIGATION OF CHEMISTRY OF N_2F_2 AND OF NOF

Thiokol
REACTION MOTORS DIVISION

Section V

INVESTIGATION OF CHEMISTRY OF N_2F_2 AND OF NOF

A. R. Young
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Report RMD AOR-ATS-63

RMD Project 5031
Report Period: 1 March 1963 to
31 December 1963

Contract No. NOnr 4079(00)
ARPA Order No. 417
Project Code 3910

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FOREWORD

This report summarizes the results of studies of N_2F_2 and NOF as potential precursors of new inorganic oxidizers during the period from 1 March 1963 to 31 December 1963 under Navy Contract NOnr 4079(00), ARPA Order No. 417.

Personnel contributing directly to these studies were A. R. Young II (Project Supervisor), D. Moy (Principal Investigator), and K. Tiger. Analytical support was contributed by R. Storey and D. Yee.

CONTENTS

CONTENTS (cont)

ABSTRACT

Attempts were made to carry out vapor phase additions to cis-N_2F_2 with NO, NO-N_2F_4 mixtures, NOF, CF_2NO, CF_3OF, CF_3NONO, NF_3O, and NO_2F. These addition reactions were attempted by both photolytic and thermal methods and under both static and flow conditions.

The flow thermal reaction of cis-N_2F_2 with NO-N_2F_4 mixtures produced a small -80°C product fraction showing major mass peaks at 68 (ONF_2^+) and 84 ($O_2NF_2^+$). Flow reactions of NO and of CF_3NO with excess cis-N_2F_2 at 230°C consistently produced small yields of liquid products which have not as yet been identified.

cis-N_2F_2 formed a 1:1 adduct with AsF_5 at room temperature. The solid adduct is stable to above 200°C. The trans-isomer of N_2F_2 did not react with AsF_5.

I. INTRODUCTION

The objective of this research program is the utilization of two unsaturated N-F compounds, N_2F_2 and NOF, as sources of new inorganic oxidizers. N_2F_2 and to some extent NOF have been neglected as subjects of synthesis research because of their marked tendencies to act as simple fluorinating agents (equations 1 and 2). This behavior is so pronounced in the case of NOF

$$N_2F_2 \longrightarrow 2F\cdot + N_2 \qquad (1)$$

$$NOF \longrightarrow F\cdot + NO \qquad (2)$$

that it is extremely difficult to carry out reactions with the pure reagent. However, recent studies of the addition of NOF to fluoroolefins and fluoroketones by Andreades (Refs 1 and 2) indicate that its chemistry may be successfully studied if great care is taken to exclude moisture and air from the reacting system and if the proper materials (Kel-F, Teflon, nickel, and Monel) are used in the construction of apparatus. Recent interest has also been shown in the chemistry of N_2F_2 by other research laboratories, an example of which is a program studying the reactions of N_2F_2 at high pressures (Ref 3).

The program at Reaction Motors Division has until the present almost exclusively involved attempts to effect free radical additions to the N=N bond of N_2F_2 and the N=O bond of NOF at atmospheric or reduced pressures. Both thermal and photolytic techniques have been employed in these attempts to demonstrate the reactivity of the unsaturated bonds in N_2F_2 and NOF. The most promising results have been obtained in studies of thermal reactions of $NO\text{-}N_2F_2$ mixtures under flow. Mass and infrared spectral data indicate that new N-F species are formed under these conditions, but as yet there is no structural evidence for the formation of addition compounds, although this is a possible course of reaction.

Other approaches to the utilization of N_2F_2 and NOF in the synthesis of new oxidizers have not been extensively explored during this nine month

period, but it is planned to evaluate some in the near future. These approaches will include:

a. The preparation of -N=NF containing compounds by controlled abstraction of fluorine from N_2F_2

b. The preparation of molecular addition compounds of N_2F_2 and NOF

c. The preparation of ionic derivatives of N_2F_2 and of NOF, such as N_2F^+ or ONF_2^-.

II. MANUSCRIPT OF PAPER FOR PUBLICATION

NONE

III. APPENDIX - INVESTIGATION OF CHEMISTRY OF N_2F_2 AND NOF

A DISCUSSION

1. Reactions of Fluorocarbon Radicals with N_2F_2

The reactivity of the N=N bond has been amply demonstrated when it is attached to groups such as R_f or -COOR. Some of the known addition reactions (Refs 4, 5, and 6) of the N=N bond are shown in equations 3 through 5.

$$3CF_3N{=}NCF_3 \xrightarrow{h\nu} CF_3{-}\underset{\displaystyle CF_3}{\underset{|}{N}}{-}\underset{\displaystyle CF_3}{\underset{|}{N}}{-}\underset{\displaystyle CF_3}{\underset{|}{N}}{-}\underset{\displaystyle CF_3}{\underset{|}{N}}{-}CF_3 + N_2 \qquad (3)$$

$$CF_3N{=}NCF_3 + CH_2N_2 \longrightarrow CF_3{-}\underset{\displaystyle N{=}N{-}CH_2}{\underset{|}{N}}{-}\underset{|}{N}{-}CF_3 \qquad (4)$$

$$ROOCN{=}NCOOR + CF_3NO \longrightarrow \underset{\displaystyle ROOCN{-}N{-}COOR}{\underset{|}{O}}{-}\underset{|}{N}{-}CF_3 \qquad (5)$$

Our earliest attempts to carry out additions to N_2F_2 employed molecules capable of producing fluorocarbon radicals. It was hoped that stable adducts having both N-R_f and N-F bonds might be formed.

a Reaction of CF_3I with N_2F_2

A 1:1 mixture of cis-N_2F_2 and CF_3I was irradiated with light from a 200 watt, quartz mercury lamp in an attempt to add CF_3 radicals to N_2F_2 (equation 6). The products obtained, however, were CF_4, C_2F_6 and N_2.

$$N_2F_2 + 2CF_3I \xrightarrow{h\nu} CF_3NFNFCF_3 + I_2 \qquad (6)$$

b. Reaction of CF_3NO with N_2F_2

The dissociation of CF_3NO into $CF_3\cdot$ and NO can be induced both thermally and photolytically. Both of these techniques were used in attempts to form an N_2F_2-CF_3NO adduct. However, the only reaction that occurred was the formation of small amounts of $(CF_3)_2NONO$. The cis-N_2F_2 was recovered in each run.

c. Reaction of $(CF_3)_2NONO$ with N_2F_2

Attempts to carry out an addition of $(CF_3)_2NONO$ to N_2F_2 (equation 7) at temperatures up to 250°C (under flow) were unsuccessful. Both reagents were recovered.

$$(CF_3)_2NONO + N_2F_2 \xrightarrow{250^\circ C} (CF_3)_2NONFNFNO \qquad (7)$$

d. Reaction of CF_3OF with N_2F_2

CF_3OF forms addition products with unsaturated organic compounds in which the $-OCF_3$ group is retained. However, an attempt to induce a similar addition to N_2F_2 (equation 8) resulted in the fluorination of N_2F_2 with N-N bond cleavage (equations 9 and 10).

$$CF_3OF + N_2F_2 \longrightarrow CF_3ONFNF_2 \qquad (8)$$

$$CF_3OF \longrightarrow CF_3O\cdot + F\cdot \qquad (9)$$

$$F\cdot + CF_3O\cdot + 1/2\ N_2F_2 \longrightarrow NF_3 + COF_2 \qquad (10)$$

2. Reactions of Nitrogen-Containing Radicals with N_2F_2

a. Reaction of N_2F_2 with $NONF_2$

$NONF_2$ is a thermally unstable, violet compound that may be prepared from NO and N_2F_4 by the method of Colburn and Johnson (Ref 7). Since it dissociates above -100°C, it is capable of providing $\cdot NF_2$ radicals at temperatures where an adduct formed by the addition of $\cdot NF_2$ radicals to N_2F_2 might be stable. NF_2 radicals could react with N_2F_2 by either of the routes shown in equations 11 and 12.

$$\cdot NF_2 + N_2F_2 \longrightarrow \cdot NFNFNF_2 \qquad (11)$$

$$\cdot NF_2 + N_2F_2 \longrightarrow NF_3 + 1/2\ FN{=}N{-}N{=}NF \qquad (12)$$

Mixtures of $NONF_2$ and cis-N_2F_2 were prepared at -196°C and allowed to warm slowly. The volatilized mixture was fractionated at -100°C and -196°C. In each run a small amount of material was retained by the -100°C trap. However, on being warmed to room temperature these fractions were found to contain NO, N_2F_2, and N_2F_4 in ratios that showed no reasonable stoichiometric relationship (NO was always in large excess) and that varied from run to run.

b Reaction of N_2F_2 with NO-N_2F_4 Mixtures

$NONF_2$ was prepared by passing a mixture of NO (excess) and N_2F_4 through an Ni tube at 230°C and condensing the effluent gas at -196°C. It was thought that a more efficient technique for carrying out the addition of $NONF_2$ to N_2F_2 than the one described in the preceeding paragraph might be to pass N_2F_2 through the heated zone along with NO and N_2F_4. On a single pass through the hot zone, an NO-N_2F_2-N_2F_4 mixture (10:2:1) gave a small product fraction (5% of initial reagents) condensing at -80°C. An infrared spectrum of this fraction showed NO, N_2O and unidentified bands in the 12 to 14μ region. A mass spectrum confirmed the presence of NO^+ and N_2O^+ fragments, along with mass peaks at 52, 66, 68, 80, 82 and 84 m/e units. Table I presents O-N-F and N-F ion fragments that correspond to these mass peaks.

TABLE I

MASS SPECTRUM OF -80°C FRACTION
FROM REACTION OF N_2F_2 WITH NO-N_2F_4

m/e	ion	m/e	ion
52	NF_2^+	80	$N_3F_2^+$
66	$N_2F_2^+$	82	$ON_2F_2^+$
68	ONF_2^+	84	$O_2NF_2^+$

A combination of ONF_2 radicals, produced as shown in equation 13, with NF_2 and N_2F_2 (equations 14 through 17) would yield products accounting for the observed mass peaks.

$$NO + N_2F_2 \longrightarrow \cdot ONF_2 + N_2 \quad (13)$$

$$\cdot ONF_2 + N_2F_2 \xrightarrow{?} F_2NO\text{-}N{=}NF + F\cdot \quad (14)$$

$$2\cdot ONF_2 + N_2F_2 \xrightarrow{?} F_2NO\text{-}NF\text{-}NF\text{-}ONF_2 \quad (15)$$

$$2\cdot ONF_2 \xrightarrow{?} F_2NO\text{-}ONF_2 \quad (16)$$

$$\cdot NF_2 + \cdot ONF_2 \xrightarrow{?} F_2N\ ONF_2 \quad (17)$$

In view of the mass spectral evidence for the possible existence of an ONF_2-N_2F_2 adduct, further studies of the thermal reactions of NO-N_2F_2 mixtures were undertaken.

c. Reactions of N_2F_2 with NO

A 2.5:1 mixture of NO and cis-N_2F_2 gave no unidentifiable products upon passage through a Monel tube at 230°C. The products obtained were: NOF, NO_2F, NO_2 and N_2O, as well as a noncondensable fraction (at -196°C).

Similarly a 1:4 mixture of NO and N_2F_2 gave on single passage through a hot Monel tube at 230°C, NO_2, NOF, NO_2F, and noncondensables, as well as unreacted N_2F_2. Upon recycling the gaseous mixture, however, a small product fraction was collected at -80°C. This fraction liquefied on warming to room temperature, and infrared and mass spectra of the vapors over the liquid indicated the presence of NO_2 and an unknown component having mass peaks at 131 and 112. These mass peaks are believed to correspond to $N_3F_3O_2^+$ and $N_3F_2O_2^+$, respectively. Various attempts to increase the yield of the liquid product have been unsuccessful. The liquid evolves NO_2 and noncondensables on standing at room temperature. The small yields as well as the instability of the liquid, have thus far frustrated efforts to characterize it.

d. Reaction of NO_2 with N_2F_2

The mass peaks at 131 observed in a product fraction of the NO-excess N_2F_2 reaction suggests an NO_2F N_2F_2 adduct. This is not unreasonable since NO_2F was observed in the products of the NO-N_2F_2 reaction. It was thought, therefore, that a significant yield of liquid product might be obtained by reacting NO_2 with cis-N_2F_2 since NO_2 would be a better precursor for NO_2F than NO. At 160°C, NO_2 was quantitatively converted to NO_2F by reaction with cis-N_2F_2 (equation 18)

$$2NO_2 + N_2F_2\ (cis) \longrightarrow NO_2F + N_2 \quad (18)$$

Although the initial NO_2-N_2F_2 mixture contained a fourfold excess of cis-N_2F_2, no liquid product was observed to form at 160°C. When the temperature of the heated zone was raised to 230°C, a small amount of condensate was trapped at -80°C. This fraction liquefied on warming to room temperature and the vapors above it exhibited 131 and 112 mass fragments, as well as NO_2^+. The yield of liquid was, however, not significantly higher than that observed in the NO-N_2F_2 reaction.

e Reactions of N_2F_2 with NF_3O in the Presence of AsF_5 and BF_3

R_fONF_2 compounds can be prepared by the addition of NF_3O to unsaturated fluorocarbons in the presence of BF_3 or AsF_5 (Ref 8). An attempt was made to carry out a similar addition reaction with cis-N_2F_2 (equation 19) in the presence of a Lewis acid catalyst.

$$NF_3O + N_2F_2 \xrightarrow{BF_3 \text{ or } AsF_5} NF_2ON_2F_3 \qquad (19)$$

Mixtures of N_2F_2-NF_3O-AsF_5 (or BF_3) in a 1:2:1 ratio were condensed into a Monel cylinder and allowed to stand at room temperature for 70 hr. The volatile phase remaining after 70 hr, in the case of the N_2F_2-NF_3O-AsF_5 mixture was predominantly NF_3O. There was no noncondensable (at -196°C) gas present, and no evidence of cis-N_2F_2 or AsF_5 by infrared absorption. However mass peaks were present at 66 and at 47 indicating the presence of trans-N_2F_2.

After removing the volatile material from the cylinder by pumping, the cylinder was heated to 250°C where it began to evolve gas. A sample of the gas was identified as cis-N_2F_2 by mass spectroscopy. It is believed that a solid adduct of N_2F_2 and AsF_5 was obtained in this run, and this possibility will be investigated further.

Upon examination of the NF_3O-N_2F_2-BF_3 mixture after 70 hours at room temperature, it was found that the initial reagents were present along with a considerable quantity of noncondensable gas.

3. Synthesis of Ionic Solids from N_2F_2

An alternate approach to the synthesis of solid inorganic N-F compounds by carrying out addition reactions at the N=N bond of N_2F_2 would be through the formation of ionic derivatives, such as $N_2F^+X^-$ or $M^+N_2F_3^-$. It is possible

that the solid compound isolated in the N_2F_2-AsF_5-NF_3O reaction (Part 2c) is an example of an N_2F^+ salt. Other attempts to prepare such derivatives have not been successful to date. These are summarized below.

a. Reaction of N_2F_2 with O_2AsF_6

An attempt was made to prepare N_2FAsF_6 via the reaction shown in equation 20.

$$N_2F_2 + O_2AsF_6 \not\longrightarrow O_2 + 1/2\ F_2 + N_2FAsF_6 \qquad (20)$$

Although some purple coloration appeared when N_2F_2 was condensed onto dioxygenyl hexafluoroarsenate at -196°C, no permanent change in the solid dioxygenyl compound was indicated when the system was warmed to room temperature. No fluorine or oxygen was evolved on allowing the reagents to stand for 20 hr at room temperature.

b. Reaction of N_2F_2 with BrF_3

No reaction occurred between N_2F_2 and BrF_3 between the melting point of BrF_3 (8.8°C) and room temperature.

4. Photolysis of N_2F_2

The ultraviolet spectrum of cis-N_2F_2 in a quartz cell shows a tail-end absorption beginning at approximately 2400 Å which reaches its maximum below 2000 Å. Since it was believed that additions to the N=N bond might be induced by vacuum ultraviolet (< 2000 Å) irradiation of N_2F_2, an apparatus was assembled as shown in Figure 1. It consists of a 200 watt hydrogen discharge tube (Hanovia-Englehard Inc.) which transmits light to 1400 Å, a Pyrex evacuation chamber, separating the lamp from the photolysis cell, and a Monel photolysis cell having a CaF_2 window.

a. Photolysis of an N_2F_2-CF_3NO Mixture in the Vacuum Ultraviolet

The initial run with the vacuum ultraviolet apparatus was made with an N_2F_2-CF_3NO mixture since it had been observed previously that these reagents did not react when irradiated in the near ultraviolet. Unfortunately the lamp developed a pinhole and burned out during the run. However, it appeared from the results of periodic infrared examination of the contents of the cell that little or no reaction was occurring between CF_3NO and N_2F_2 up to the time when the lamp burned out (approximately 2 hr).

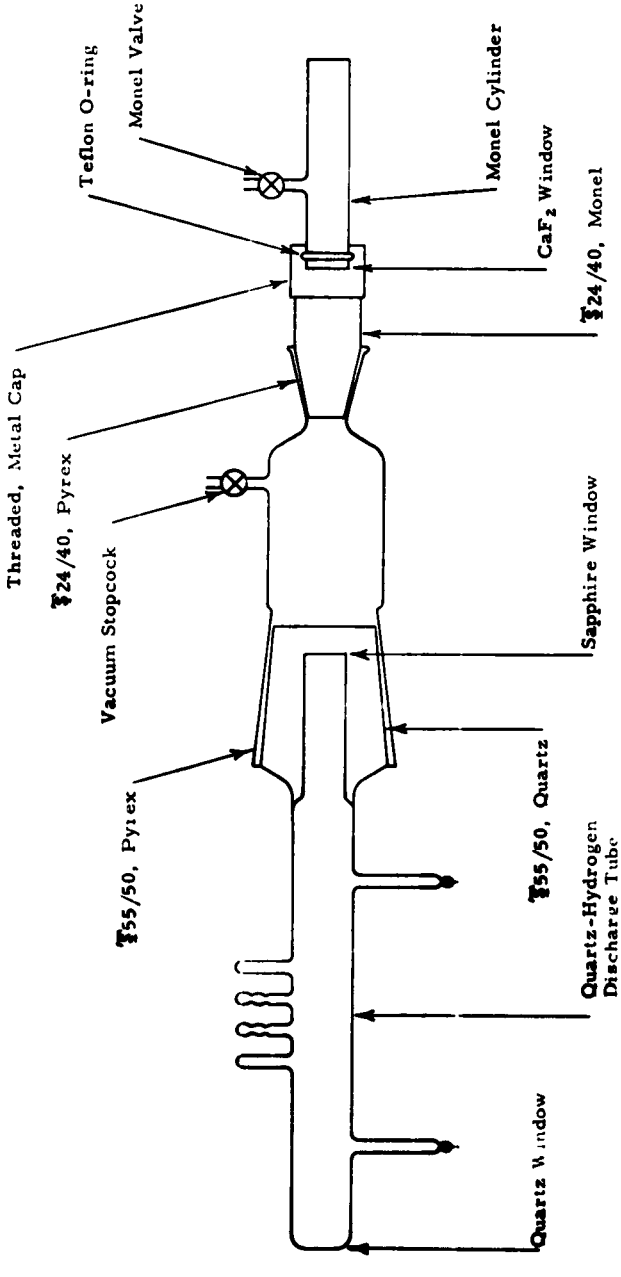

Figure 1. Apparatus for Photolysis Studies in Vacuum Ultraviolet

b. Photolysis of an $NOF-N_2F_2$ Mixture

An equimolar mixture of NOF and N_2F_2 contained in a Monel infrared cell with CaF_2 windows was irradiated for 40 hr with light from a quartz-mercury lamp. The starting reagents were converted to NO, N_2O, NO_2 and noncondensables. There were also traces of CO_2, COF_2, and CF_4, the presence of which indicates a small air leak during the run.

c. Photolysis of an $NF_3O-N_2F_2$ Mixture

The irradiation of an equimolar mixture of NF_3O and cis-N_2F_2 for two hours produced some NOF. Since the intensity of the cis-N_2F_2 absorption at 6.5μ was little changed, the reaction probably only involved photodecomposition of NF_3O (equation 21).

$$NF_3O \xrightarrow{h\nu} NOF + F_2 \qquad (21)$$

5. Reactions of NOF

The reactions of NOF were not investigated as extensively as planned because of difficulties encountered in preparing reasonably pure samples of NOF. At the beginning of the program, we prepared NOF by the pyrolysis of $NOBF_4$ in the presence of NaF. This procedure gave a product containing from 20 to 50% NO_2 until the various precautions described below were taken. Later in the program it was found more convenient to generate NOF from commercially available NOF·3HF, a liquid complex.* Using the same precautions necessary to obtain a reasonably pure product from $NOBF_4$, we obtained samples of NOF containing only a trace of NO_2 by infrared analysis.

a Preparation of Pure Nitrosyl Fluoride

A convenient laboratory method for the preparation of large quantities of NOF without the use of large amounts of fluorine is by the pyrolysis of a mixture of $NOBF_4$ and NaF (equation 22).

$$NOBF_4 + NaF \xrightarrow{250^\circ C} NOF + NaBF_4 \qquad (22)$$

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* NOF·3HF can be obtained from the Ozark-Mahoning Company, Tulsa, Oklahoma.

The success of this method, however, depends on the care with which air and moisture are excluded from the apparatus and on the passivation (formation of fluoride coating) of any metal surfaces in the apparatus. It is necessary that only nickel or high nickel content alloys be used in the construction of apparatus for handling NOF.

The most prevalent impurity in NOF samples prepared by the reaction shown in equation 22 is N_2O_3. This impurity usually arises by the reaction of NOF with moisture (equation 23).

$$2NOF + H_2O \longrightarrow 2HF + N_2O_3 \qquad (23)$$

It is virtually impossible to remove appreciable quantities of NO and NO_2 from NOF by conventional trap-to-trap distillation. Small samples of NOF (less than a millimole) can be purified by gas chromatography on a single pass, but this method is not practical for the purification of large amounts of the reagent. It is, therefore, necessary to make sure that minimum formation of NO and NO_2 occurs during the preparation. This requires that the $NOBF_4$ and NaF be scrupulously dried prior to pyrolysis, that the metal system be passivated in order to prevent the formation of NO ($NOF + M \longrightarrow MF + NO$), and that the system be free of air leaks. By following these precautions NOF, which shows only a trace of NO_2 by infrared analysis, has been prepared on a 0.1 to 1.0 molar scale and it has been shown that some, if not all, of the NO_2 arises by decomposition of the sample in the infrared cell. More recently, good samples of NOF have been prepared by the reaction of $NOF \cdot 3HF$ with NaF at room temperature.

b Reaction of NOF with C_2F_4

NOF underwent a complex reaction with C_2F_4 between -40°C and room temperature. The principal products were C_2F_5NO, CF_3NO, and a viscous liquid having an infrared spectrum quite similar to that of samples of nitroso rubber. The nitroso rubber was probably formed by reaction of the R_fNO compounds with C_2F_4.

c Reaction of NOF with N_2F_2

A flow reaction of NOF and N_2F_2 (in equimolar quantities) at 230°C produced principally noncondensables and NO_2, but there was a small fraction retained at -80°C which liquefied on warming to room temperature and appeared to be the unidentified liquid product obtained by the reactions of NO or NO_2 with excess N_2F_2.

B. EXPERIMENTAL

1. Reactions of cis-N_2F_2 with Fluorocarbon Radicals

a. Preliminary Photolysis Studies Monitored by Mass Spectroscopy

A Bendix Time-of-Flight Mass Spectrometer (Model 12-100) equipped with a Model S-14 ion source was used to study some photolytic reactions of cis-N_2F_2 with sources of fluorocarbon radicals. The Model S-14 ion source provides an inlet for a molecular leak approximately 3 mm behind the ionizing beam. The ion chamber was fitted with a quartz lens to permit transmission or radiation from a quartz-mercury arc lamp.

An initial experiment was carried out with pure CF_3I in order to check out the operating procedure and apparatus. CF_3I was irradiated in the fast reaction chamber using 5 mm and 20 mm pressures in the reaction chamber. The observed products from the reaction were I_2 and C_2F_6. In the experiment using 20 mm pressure, increases in m/e 69 (CF_3^+), 50 (CF_2^+), 31 (CF^+), and 12 (C^+) were observed which were indicative of the presence of $CF_3\cdot^+$ and/or CF_4. No apparent increase in m/e 119 ($C_2F_5^+$) due to C_2F_6 was observed, eliminating the possibility of any contribution of C_2F_6 to the 69, 50, and 31 mass peaks.

Further fast reaction studies were made using N_2F_2, CF_3I-N_2F_2, and CF_3NO-N_2F_2 mixtures. N_2F_2 at 8 mm pressure in the reaction chamber was irradiated with and without a Pyrex shield between the ultraviolet source and the quartz lens. No change was observed in the spectrum in either experiment after one hour irradiation periods.

A mixture of CF_3I and N_2F_2 in a 1:1 ratio was irradiated both with and without a Pyrex shield. In the experiment using the Pyrex shield, no change was observed in the mass spectrum obtained even after one hour. C_2F_6 and I_2 were observed immediately upon removing the Pyrex shield. The N_2F_2 content of the mixture was then increased to give a 1:2 ratio of CF_3I to N_2F_2. A small mass peak then appeared at m/e 97 which corresponds to $CF_3N_2^+$.

Mixtures of CF_3NO and N_2F_2 in a 1.5 ratio at total pressures of 10 mm and 40 mm, respectively, were irradiated for five hour periods with no evidence from mass spectroscopy of interaction between the two reagents.

b Photolysis of CF_3NO and N_2F_2

CF_3NO (5mmoles) and N_2F_2 (5 mmoles) were irradiated in a 1-liter Pyrex bulb overnight with near ultraviolet light. Fractionation at -120°C and -160°C allowed identification of the dimer, $(CF_3)_2NONO$, as the only product.

c Reaction of $(CF_3)_2NONO$ and N_2F_2

$(CF_3)_2NONO$ was prepared by visible and ultraviolet irradiation of CF_3NO in a 1-liter Pyrex bulb for 72 hr. It was purified by a low temperature vacuum distillation and identified by its infrared spectrum. $(CF_3)_2NONO$ (3mmoles) and 6 mmoles of N_2F_2 were passed through a hot tube at 150°C. The gases were fractionated at -80°C and -160°C but no new products were identified. A second run was conducted with the Monel tube at 250°C. Similar results were obtained at the higher temperature.

d Reaction of CF_3OF and N_2F_2

CF_3OF was prepared by the fluorination of sodium trifluoroacetate in Pyrex at room temperature with nitrogen-diluted fluorine. The product was separated from COF_2 and C_2F_6 by low temperature vacuum distillation. The final product probably contained traces of SiF_4, $(CF_3)_2CFOF$ and CF_3CF_2OF. At room temperature, 1 mmole of CF_3OF and 1 mmole of N_2F_2 were left in contact overnight in a Monel cylinder. Fractionation of the mixture at -160°C showed COF_2 in the CF_3OF fraction. The detection of NF_3 or N_2F_4 was uncertain because of the small amounts involved.

A mixture of 2.5 mmoles of N_2F_2 and 1 mmole of CF_3OF was passed through a hot tube at 160°C. Fractionation at -100°C and -160°C showed NO_2 in the -100°C bath and COF_2 in the -160°C trap, along with NF_3 and N_2F_2.

2 Reactions of N_2F_2 with Nitrogen-Containing Radicals

a $NONF_2$ and N_2F_2

A 7:1 mixture of NO and N_2F_4, respectively, was passed through a hot Monel tube at 250°C and the resulting gases condensed immediately at -196°C. Unreacted NO was removed by pumping on the collection trap after warming it to -160°C. N_2F_2 (3.2 mmoles) was condensed on 6.4 mmoles of the $NONF_2$ at -196°C. The -196°C bath was removed, and the expanding gases were passed through a -100°C bath into another -196°C bath. More than 95% of the gases (on the basis of the original pressures) was recovered at -196°C. NO, N_2F_2,

and N_2F_4 were identified by mass spectral analysis, along with traces of NO_2 and NF_3. On warming the -100°C trap to room temperature, 0.2 mmole of gases was collected in the -100°C bath. However, after this gas had remained at room temperature for 15 minutes, it was no longer condensable at -100°C. Mass spectral analysis identified NO, N_2F_2 and N_2F_4, in approximately an 8:1:1 ratio, along with traces of NO_2 and N_2O.

b. NO, N_2F_4 and N_2F_2

A 1:2:10 mixture of N_2F_2:N_2F_4:NO, respectively, was passed through a hot Monel tube at 230°C. Fractionation of the gases gave > 95% of the starting materials, with a small amount of noncondensable gases. A small portion of product was stopped at -80°C and infrared and mass spectral analyses showed traces of HNF_2, N_2O, and appreciable quantities of NO. Furthermore, there were unidentified bands in the 12 to 14μ region of the infrared spectrum and unidentifiable mass peaks at 66, 68 and 84 m/e (major peaks) and at 80 and 82 m/e (minor peaks).

c. NO and cis-N_2F_2

A 2.5:1 mixture of NO and N_2F_2 was passed through the hot Monel tube at 230°C on a single pass. The reacting gases were condensed immediately at -196°C. A large amount of noncondensable gases (at -196°C), corresponding to approximately 50% of the original pressure, was generated. Fractionation of the reacting gases at -110°, -160° and -196°C showed unreacted NO, N_2O and N_2F_2 in the -196°C fraction and NOF, NO_2F and N_2O_3 in the -110 and -160°C fractions

The ratio of NO:N_2F_2 was then changed to 1:4 and the mixture was repeatedly passed through the heated tube at 230°C. Appreciable amounts of noncondensable gases (approximately 30 to 50% of the starting pressures were formed). After repeated passages, fractions of the resulting materials showed NOF, NO_2F and NO_2 (no cis N_2F_2) among the highly volatile products and a small amount of a liquid with a relatively high freezing point. The material was a solid at dry ice temperature (-80°C) and melted at approximately -30°C. The melting point could not be determined with any degree of certainty since the material seemed to be decomposing above -80°C. The vapors at room temperature showed the normal infrared spectrum of NO_2, along with unidentified absorption at 9.75μ and 14μ. (The structure of this band was poorly resolved because of the low intensity and/or the low concentration of material.)

The mass spectrum showed mass peaks of 30 and 46 (NO^+ and NO_2^+), as well as mass peaks at 112 and 131 m/e units. Appreciable amounts of HF (20 m/e) and what appeared to be C-F material (69-CF_3^+) was also observed

In these runs numerous flashes were encountered as the gases (after passing the hot tube) were pumped through a -196°C trap. On one occasion, the -196°C trap detonated while the noncondensable gases were being pumped through.

d. NO_2 and cis-N_2F_2

A 4:1 mixture of N_2F_2 and NO_2 was circulated through the hot tube at 160°C with almost complete conversion to NO_2F. Noncondensable gases (at -196°C) were also obtained Continued circulation through the hot tube (at temperatures ranging from 200 to 250°C) gave a small amount of the liquid product described in the two previous sections. NO, NO_2 and NO_2F were identified in the vapor and the liquid showed ion fragments with 112 and 131 m/e units.

e. NF_3O and cis-N_2F_2 in the Presence of AsF_5 or BF_3

NF_3O, AsF_5 (or BF_3) and cis-N_2F_2 were separately condensed into a Monel cylinder in a 2:1:1 ratio, respectively. The cylinder was allowed to warm to room temperature and remained at that temperature for approximately 70 hr.

Reaction A

The vapors in reaction A, which employed AsF_5, were analyzed by infrared and mass spectrometry. Only NF_3O could be positively identified by the infrared spectrum, although the mass spectrum showed strong 47 and 52 peaks At this time, it cannot be determined definitely whether these peaks were due to cis-N_2F_2 and N_2F_4 or a new product. The cylinder was heated and pumped on at 250°C. A small amount of gas was evolved and its mass spectrum showed the presence of SiF_4 and NO and a strong 47 m/e peak, indicating N_2F_2.

Reaction B

Reaction B, using BF_3, showed only unreacted starting materials in the vapor, along with a large amount (approximately 40%) of noncondensable gases (at -196°C).

3. Reaction of cis-N_2F_2 with O_2AsF_6

A 0.3 mmole sample of O_2AsF_6 was weighed under dry nitrogen into a round bottom flask with stopcock-ball joint assembly and attached to a glass vacuum system. The flask was evacuated, cooled to -196°C, and 0.3 mmole cis-N_2F_2 was condensed into the flask. The flask was isolated from the vacuum system by closing the stopcock and was warmed to -80°C. A violet color formed on the surface of the solid O_2AsF_6. The violet color was present after 24 hr at -80°C, but upon warming the system to room temperature no noncondensable gas was liberated. The same result was obtained when the system was allowed to stand at room temperature for 24 hr.

4. Reaction of cis-N_2F_2 with BrF_3

cis-N_2F_2 was condensed into a 25 ml Kel-F tube containing 5 liquid ml BrF_3. The system was allowed to warm to the melting point of BrF_3 (approximately 9°C). No solid formation was observed at 9°C. The pressure of N_2F_2 (500 mm) over the liquid BrF_3 remained virtually constant over a 24 hr period at room temperature.

5. Photolysis Studies with cis-N_2F_2

a. N_2F_2 and CF_3NO in Vacuum Ultraviolet

A 1:1 mixture of CF_3NO and N_2F_2 was expanded into the Monel photolysis cell (Figure 1) at a total pressure of 50 mm. The cell was irradiated from the hydrogen discharge arc source, the light being transmitted through the sapphire window on the discharge lamp (Figure 1), the evacuated Pyrex chamber, and the CaF_2 window on the Monel cell. Infrared spectra were obtained after three and eight hours, and showed little change in the absorptions due to CF_3NO and cis-N_2F_2. However, there was a trace of COF_2 apparent in the spectra. Upon continuing the irradiation of the sample overnight, a pinhole developed in the discharge tube causing it to burn out.

b. Photolysis of NOF-cis-N_2F_2

An equimolar mixture of NOF and cis-N_2F_2 at a total pressure of 100 mm was expanded into a Monel infrared cell having CaF_2 windows. Upon irradiating this mixture for 40 hr with a quartz-mercury arc lamp, the contents were examined by infrared from 2-10μ. The spectrum showed some of the initial N_2F_2 to be still present, along with N_2O, NO_2, NO; there were also traces of CO_2, COF_2, and CF_4. The NOF had been completely consumed.

c. Photolysis of NF_3O-cis-N_2F_2

An equimolar mixture of NF_3O and cis-N_2F_2 (100 mm total pressure) was irradiated in a Monel infrared cell for 2 hr by means of a quartz-mercury arc lamp. The infrared spectrum (from 2 to 10μ) of the contents of the cell indicated little change in N_2F_2 concentration, the disappearance of some NF_3O and the appearance of NOF.

6. Reactions of NOF

a. NOF and cis-N_2F_2

A 1:1 mixture of NOF and cis-N_2F_2 was passed once through the Monel tube at 230°C. A liquid product similar to that described above was obtained in very small yield. In the vapors, unreacted NOF and cis-N_2F_2 were identified along with NO_2 and NO_2F.

b NOF and C_2F_4

Equimolar amounts of NOF and C_2F_4 were condensed into a Monel cylinder at -196°C and maintained at -42°C for 10 days. The NOF was completely consumed. Some C_2F_4 was recovered but there was also present a complex mixture of fluorocarbon products, including nitroso compounds (CF_3NO, C_2F_5NO), nitrates (R_fONO), and a carboxylic acid. There was also a small quantity of viscous liquid which appeared from the infrared analysis to be a copolymer of CF_3NO and C_2F_4.

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